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Chemical Vapor Synthesis of High-Quality Centimeter-Sized Crystals of Monolayer Graphene

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Chapter 1

Scientific and technological motivations

Graphene is a two-dimensional monolayer composed of carbon atoms tightly packed into a hexagonal lattice. Although graphite, its 3-D counterpart, has been used for several centuries by humankind, graphene was not discovered until 2004 in its isolated, observable and testable form. This single sheet was first obtained by two Russian condensed-matter physicists, K. S. Novoselov and A. K. Geim at the University of Manchester who noticed that exceptionally thin fragments could be peeled off of a graphite piece. Continuously peeling the layers from the graphite fragment eventually lead to the isolation of a crystalline material with a thickness of just one atom [1]. The groundbreaking experiments they conducted on graphene revealed a series of unique electronic properties that sparked such a great deal of interest among the research community that the Royal Swedish Academy of Sciences decided to award them the Nobel Prize of Physics in 2010.

Ensuing theoretical and experimental studies further contributed to the graphene renown by revealing that, in addition to the amazing electronic properties such as charge carrier mobilities as high as $200\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 5K [2], graphene also possesses other interesting physical properties

including a stiffness higher than steel (Young's modulus 1TPa) [3, 4], a thermal conductivity substantially higher than diamond (up to 5000 W.m⁻¹.K⁻¹) [5], the ability to absorb 2.3% of visible light [6], an amazing impermeability to most gases and liquids [7], an unprecedented flexibility [8] and, the ability to sense a wide range of species and conditions such as humidity, temperature and even electromagnetic radiation [9–11].

Context

This unrivaled combination of properties inspired scientists from both academia and industry to incorporate graphene into a wide range of practical applications spanning over various fields: energy storage (batteries, super capacitors) [12, 13] and harvesting (geometric diodes, solar cells) [14, 15], coatings (anti-corrosion, conductive inks) [16], health (drug delivery, faster DNA sequencing, smart plasters, healthcare monitors) [17, 18], sensing (pressure, temperature, atmosphere composition, radiation) [19, 20], filtration (desalination, purification) [21, 22], composites [23] and flexible or high-frequency electronics (flexible ultra-thin displays, touch screens, RFIDs, transistors) [24–27].

In this context, graphene is considered of particular interest in the field of information technology, which has been exponentially developing since the advent of the internet and personal computers in the late 1980s and early 1990s. Nowadays, the number of internet users currently exceeds 3 billion people and more than half of them are primarily connecting via their smartphones. Smartphones that were, for instance, reserved for the wealthy elite about 20 years ago are now in everyone's pockets as more than 200 million units are sold every 3 months. Besides reducing their prices, electronic devices are getting smaller and feature an ever increasing processing power. This technological trend reflects the well-known Moore's law postulating that computing power, roughly estimated by the number of transistors that can be embedded in a single processor chip, approximately doubles every 18 months [28]. This trend which has been a real driving force for the semiconductor industry and somehow helped surpassing physical, chemical and manufacturing challenges, is progressively fading away.

Presently, companies like Intel are able to mass-produce processors with 10-nanometer-long transistors, which is getting close to the physical limit of which silicon-based transistors are able to shrink [29,30]. The semiconductor industry thus has no choice but to turn to other materials with appropriate electronic properties and whose dimensions can be controlled at the atomic scale. Although graphene cannot be directly of great assistance for logic electronic applications due to the absence of band-gap, it is of great interest for extending the service life of mobile devices and diversifying/broadening the range of electronic applications.

Unfortunately, there are several challenges to be addressed before being able to exploit graphene's fantastic properties in practical technologic applications. The main challenge lies in producing large quantities of graphene with a high throughput, structural quality and chemical purity at an affordable price. Graphene can currently be produced by a multitude of methods that can be classified in two categories: "bottom up" approaches that use chemical reactions (graphitization) to synthesize graphene from other carbon sources and "top-down" approaches which are based on the processing of bulk graphite. The production yield, structural quality, chemical purity and the "format" of graphene strongly depend on the employed production method.

Top-down approaches for instance can yield several kilograms of graphene derivative in one single batch and for a relatively low cost. Given that graphite is a relatively abundant material on earth and that the production throughput is directly proportional to the initial amount a raw graphite, this approach can be furthermore scaled-up. However, the various reported separation processes including arc discharge [31,32], exfoliation of graphene oxide [33], electrochemical exfoliation [34], exfoliation of intercalation compounds [35,36] and solvent-based exfoliation [37,38], can only produce small graphene fragments, have a relatively poor control over the number of layers, often employ hazardous chemicals and drastically compromise the physical integrity and chemical purity of graphene. Nevertheless, the resulting graphene powder or suspension can be of great use for applications such as composites in order to make materials stronger or electrically conductive, printed

electronics, super capacitors and filtration applications.

Bottom-up approaches on the other hand, such as chemical vapor deposition (CVD) or epitaxial growth on silicon carbide (SiC), offer large surface areas of graphene with a high chemical purity, a relatively high structural quality and a better control over the number of layers. Counterbalancing these advantages, the production cost of graphene from SiC is very high compared to the other methods as high-quality SiC wafers are quite expensive to produce and the sublimation of silicon required to grow graphene occurs at very high temperature (~ 1200 - 1700 °C) [39–42]. Although graphene-based electronic devices can directly be produced on the SiC synthesis substrate because of its insulating nature, it is rather challenging to transfer graphene onto other surfaces, thus reducing the spectrum of potential applications [43]. In contrast, chemical vapor deposition of graphene has been demonstrated using various synthesis substrates, requires a lower processing temperature (~ 600 - 1080 °C) and can be transferred on pretty much any kind of surface, which make it the most promising manufacturing method for the realization of practical high-performance applications.

Objectives of the thesis

This research mainly focuses on developing tools allowing the production of large-area high-quality graphene with a controllable number of layers and fostering its integration in potential advanced technological applications. This thesis thus involves (i) studying various types of Cu substrates that are used as catalyst for the synthesis of graphene but can also be employed as a platform for the realization of devices, (ii) devising a chemical vapor deposition setup that can reach a wide range of parameters and thus offering new possibilities in terms of graphene growth conditions, (iii) improving the understanding of fundamental graphene growth mechanisms indispensable for the production of graphene with minimal crystalline defects and, (iv) developing an efficient and reliable method for transferring graphene onto desired device-compatible substrates.

Thesis outline

This thesis is organized as followed:

Chapter 2 starts with reviewing the various graphene chemical vapor deposition (CVD) procedures that have been reported so far. After introducing the basic graphene growth mechanisms and demonstrating why copper is considered as the most promising synthesis substrate for the growth of graphene, this chapter presents the great advances developed by the scientific community in order to improve the controllability of the CVD process over the structural quality and the number of layers.

Chapter 3 presents the CVD setup that was initially used at the early stage of this research and exposes the different catalyst alternatives that have been investigated. As transferring graphene is essential for characterization and device fabrication purposes, this chapter also gives a detailed account of the procedure employed to transfer large-area graphene on arbitrary surfaces. Finally, the various characterization tools that have been employed on a daily basis to assess graphene's structural quality and number of layers are presented.

Chapter 4 shows the first graphene growth results that have been obtained with the initial CVD setup and points out the various scientific and technological challenges that had to be addressed in order to reach state-of-the-art graphene production. Aside from demonstrating that the currently used CVD setup is limited and unable to directly achieve graphene growth results with a quality similar to what is reported in the literature, this chapter shows that decent graphene results can however be achieved by confining the Cu surface with an inert material. The role of Cu surface confinement is then further discussed and put into context with similar observations reported in the literature.

In order to address the limitations presented in chapter 4, various CVD setup modifications have been made over the years in order to explore a wider range of CVD parameters, improve the graphene growth results and achieve better repeatability and reproducibility of the experiments.

Chapter 5 exposes these modifications that, at first sight, seem to

address more technical and technological issues, but represent the keystone of the advanced CVD results presented in chapters 6 and 7.

Chapter 6 exploits the customized CVD setup capabilities, and more particularly the ability to precisely adjust the global pressure inside the CVD chamber as the CVD protocol proceeds. This particular feature, which was first employed to systematically study the impact of CVD protocol conditions on the growth of graphene, has been found to be essential to produce millimeter-size single-crystals of graphene on a 3-inch Cu film wafer.

Using appropriate pre-growth conditions represents one of the key factors enabling the production of graphene domains with lateral dimensions going beyond the state-of-the-art of graphene synthesis on Cu film. Unfortunately, the spectrum of investigation for the pre-growth conditions is relatively limited given that the quasi-2D nature of the Cu film makes its physical integrity more sensitive to the harsh CVD pre-growth environment. **Chapter 7** thus presents additional experiments that have been achieved using Cu foils as catalyst in order to further uncover the full potential of pre-growth conditions in controlling graphene growth.

Finally, **Chapter 8** summarizes the major scientific findings and proposes a series of perspectives for additional research in the field of graphene growth, transfer and device fabrication.

Chapter 2

Literature review of CVD Growth

Presently, chemical vapor deposition (CVD) on copper is the most technologically advanced graphene manufacturing approach as it yields continuous large-area graphene films with a controllable number of layers. Unfortunately, CVD-grown graphene usually exhibits a lower structural quality than the pristine material obtained by mechanical exfoliation of graphite. The poor graphene quality is known to adversely impact its physical properties and must be improved in order to fully exploit graphene's high potential once integrated into functional devices.

Section 2.1 explains the underlying physical background of CVD growth, fits the methane-based CVD growth into the framework of other existing graphene CVD approaches, and shows the benefits of using Cu compared with other synthesis substrates. Then, Section 2.2 and 2.3 present the various approaches that have been developed over the past 8 years in order to address the structural quality limitations, better control the number of layers and ensure a high uniformity over large areas. Finally, section 2.4 discusses the primary challenges stemming from the use of Cu films instead of the widely employed Cu foils as catalyst for the CVD growth of graphene.

2.1 Fundamentals of CVD growth of graphene

The chemical vapor deposition (CVD) process consists of depositing a solid material using a vapor precursor which chemically reacts on or in the vicinity of a synthesis substrate surface upon heating at high temperature. Although this technique has been widely used in the semiconductor industry for the deposition of materials such as polysilicon and silicon nitride, its application towards graphene synthesis was not demonstrated before 2008 [44]. The discovery of a non-expensive and scalable graphene manufacturing technique sparked a great deal of interest among the scientific community and in the industry. In that respect, the past 8 years have seen a tremendous increase of research activities focusing on improving the controllability over the CVD production process. Consequently, the literature flourished with a multitude of process variants including different synthesis substrates, carbon precursors, and whether particular methods are used to activate the graphene formation reaction.

Up to now, graphene has been synthesized on a wide variety of substrates including metals [45], semiconductors (Ge [46,47]) and insulators (Al_2O_3 [48], Si_3N_4 [49, 50]). In terms of structural quality and control over the number of layers, the best CVD synthesis results have been achieved using transition metals including Co, Cu, Fe, Ir, Ni, Pt and Ru. These metals have the ability to catalyze the chemical vapor deposition meaning that they provide a lower energy pathway for both the decomposition of the carbon precursor into adsorbed C-based species and the graphitization reaction by stabilizing graphene. This stabilization mainly comes from the ability of transition metals to form intermediate soft bonds with graphene. In the case of Cu, for instance, π electrons from the $2p_z$ orbitals of C atoms are shared with the partially filled $4s$ orbitals of Cu atoms. Moreover, using a catalyst leads to the heterogeneous decomposition of the carbon precursor on the desired surface and prevents the formation of carbon aggregates in the gas phase (e.g. soot) or on the CVD reactor inner walls.

Depending on the employed catalytic material, the fundamental graphene growth mechanisms and thus the control over the graphene structural quality and number of layers can significantly differ. This disparity mainly arises from variations in the catalytic activity, the carbon solubility and the carbon affinity of the catalyst when heated up at high temperature. In order to explain their experimental CVD synthesis results on Cu catalyst, a few research groups proposed rather similar mechanisms for the growth of graphene which involve the following key stages [51–54]:

1. Breakdown of the carbon precursor on the catalytic surface through dissociative adsorption to form active C-based species $(\text{CH}_{x \leq 4})_s$ where "s" stands for the surface-adsorbed species in opposition to the gaseous molecules.
2. Competition between the adsorption, desorption and diffusion of active species $(\text{CH}_{x \leq 4})_s$ on the catalyst surface. These species tend to aggregate together to form more stable clusters $(\text{C}_n\text{H}_y)_s$ that can potentially become stable graphene nuclei.
3. Once a certain amount of graphene nuclei is formed, the freshly adsorbed active C species tend to chemically react with existing graphene islands and contribute to their development rather than forming additional nuclei. As the graphene growth proceeds, the graphene nuclei develop to become graphene islands (also called domains, grains or flakes) that will eventually merge together to form a continuous graphene film.

Although the exact nature of the adsorbed active C species has not been well identified yet, theoretical calculations predicted that the complete dehydrogenation of hydrocarbons such as methane into atomic carbon is energetically very unfavorable on the Cu surface [55]. The aforementioned mechanism implies that adsorbed active C species are virtually constrained on the catalyst surface where they can diffuse and react with growing graphene domains. This surface-mediated process only applies to metals having a very low carbon solubility such as Cu and Pt. For

other metals that exhibit a higher C solubility such as Ni and Co, the active C species also diffuse on the surface but a significant amount of them dissolves into the catalyst bulk upon the exposure to high temperature. Due to the C solubility temperature dependency, dissolved C species tend to out-diffuse, precipitate at the surface and produce additional graphene layers upon the cooling phase of the CVD protocol. Compared with the surface-mediated process, the bulk-mediated process is thus far more complex due to additional key process parameters for the graphene growth such as the C concentration of the catalyst, the catalyst thickness and the cooling rate. Moreover, dissolved C species preferentially out-diffuse through the catalyst grain boundaries and consequently produce additional layers that are essentially localized near the catalyst grain boundary grooves. Metals with an even higher carbon affinity such as Fe can also result in the formation of carbide phases upon the high temperature CVD process, which makes the CVD growth of graphene even more complex than with other metals [56,57]. It is therefore essential to employ a low C solubility substrate when the uniformity and the control over the number of layers are of central importance¹. Because of its low carbon solubility and its moderate catalytic activity, copper is considered as a top candidate for being used as a synthesis substrate for graphene growth. Given that graphene is impermeable to gases, the growing graphene domains inhibit the adsorption of C precursors on the Cu surface underneath. Once the graphene sheet entirely covers the catalyst, the C supply is suppressed and the graphene growth process stops by itself. The growth of graphene on Cu catalyst is thus referred to as a self-limited process. Bi- and few-layer graphene regions can however grow on the Cu catalyst if the active C species can diffuse on the surface under the first growing layer without being attached on the top layer domain edge [62].

Directly synthesizing graphene onto electrical insulating materials such as sapphire or silicon dioxide would be very attractive for the development of graphene-based devices and the co-integration of graphene

¹The C solubility of Cu, Pt, Ir, Ru and Ni are ~ 0.0007 , ~ 0.005 , ~ 0.07 , ~ 0.5 and ~ 1 at.%, respectively at 1000 °C [58–61].

with the CMOS platform. Due to the absence of catalytic activity of these materials, other strategies have been developed to facilitate the decomposition of C precursors on the substrate surface such as higher growth temperatures ($T \sim 1350$ °C), plasma-enhanced CVD or more reactive C sources. Although tremendous efforts have been dedicated in this regard, catalyst-free CVD processes have only produced poor quality graphene so far [48, 63, 64].

Since the first demonstration of CVD growth of graphene that was based on the chemical reaction of methane, several other substances have been investigated including alcohol vapors (methanol [65], ethanol [65, 66], propanol [65]), hydrocarbons (acetylene [67], ethylene [68], benzene [69], oil [70]) or even vapors obtained by the pyrolysis or vaporization of solid polymers (polystyrene [71], PMMA [72], coronene [73]), plants [63], insects or food [74]. Methane is often preferred over other C sources because it is a very stable molecule (with strong C-H bonds) and thus requires very high thermal energy ($T \geq 1200$ °C) to be thermally decomposed without catalyst [52, 75]. Therefore, it only decomposes on the catalyst surface and does not react in the atmosphere of the CVD furnace or on the top surface of growing graphene. Using more reactive precursors negatively impacts the control over the number of layers and the quality as they result in an excessive adsorption of C based species on the catalytic surface.

Because the production of a uniform graphene sheet with minimal crystalline defects and a controllable number of layers is highly desirable for its integration in advanced technological applications, intensive efforts have been devoted to improve the controllability over the growth process using methane as carbon source and Cu substrates as catalysts. Owing that the CVD growth of graphene on Cu is a surface-mediated and self-limited process, the growth of graphene is limited to a few layers and the uniformity of the deposition deals more with gas flow dynamics over the catalytic surface rather than actual CVD conditions. The scientific community thus predominantly focused on improving the structural quality which is essential for achieving graphene's exciting physical properties. Unfortunately, CVD-grown graphene falls short in terms of

structural quality compared to its exfoliated counterpart for 3 reasons. First, graphene formation results from the the nucleation, growth and coalescence of single-crystalline graphene domains (GDs). Because the graphene lattice in-plane orientation varies from one domain to another, the junction of adjacent graphene domains creates defect lines called graphene grain boundaries (GGBs) [76, 77]. Defects in graphene's lattice can also appear during the growth of individual graphene domains due to the presence of impurities, dopants or simply because of inappropriate CVD conditions which lead to a poor graphitization. Finally, as graphene growth mimics the underlying Cu surface morphology, topological features on the Cu surface are accommodated by the presence of topological defects and out-of-plane deformations in graphene [77].

The two next sections describe the major experimental advances that have been made in the field of CVD growth of graphene using a Cu catalyst and methane as carbon source. Cu foil is the most widely used form of Cu catalyst being employed for exploring strategies to improve graphene's structural quality or for studying fundamental growth mechanisms (section 2.2). On the other hand, using Cu films represents a real asset for application purposes and fundamental studies as shown in 2.3.

2.2 CVD of graphene on copper foils

Given that it is very challenging to control the Cu surface morphology at the micro- and nanoscale upon the high temperature CVD process, the main advances that have been made in this area concern the improvement of the crystalline structure of growing domains and the reduction of GGB-induced defects. Up to now, three major strategies have been investigated to address these limitations: controlling the size, the location and the lattice orientation of growing single-crystalline GDs.

2.2.1 Race for the growth of large graphene domains

The best approach to suppress GGB-induced defects consists of producing graphene sheets made of larger GDs and thus containing a lower GGBs density. This approach, introduced in 2010 by Li *et al.* [78], triggered a race among the scientific community towards the development of methods leading to ultra low nucleation site density at the earlier stage of graphene growth. In that way, single-crystalline GDs can expand over large areas before coalescing with each other. Producing GDs with compact shapes also contributes to the reduction of the GGBs density as dendritic domains form jagged defect lines when they merge together. In this regard, the past 7 years have seen a substantial increase of interest in techniques leading to this goal including the proper tuning of CVD parameters, Cu foil pretreatments, customized Cu foil geometries and non-conventional CVD furnace configurations. These four approaches are described in some more details in the following paragraphs.

Appropriate CVD conditions

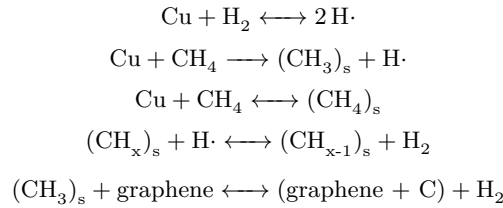
The employed CVD processing parameters, and more particularly the CVD conditions present in the vicinity of the Cu surface such as the methane partial pressure (P_{CH_4}), the hydrogen-to-methane ratio (R), the global pressure (P) and the growth temperature (T_{gr}) play a crucial role in determining the domain density and shape.

Li *et al.* [78] first discovered that changing the growth temperature of the LPCVD process from 985 to 1035°C and the methane partial pressure from 0.61 to 0.21 mbar was increasing the lateral size of graphene domains from $\sim 5\ \mu\text{m}$ to $\sim 25\ \mu\text{m}$. These observations were corroborated later by Jia *et al.* [79] who further decreased the P_{CH_4} to obtain 100- μm -large graphene domains. Zhang *et al.* [80] employed a 5% Ar/ CH_4 gas mixture as C-source feedstock to better control the P_{CH_4} injected in the furnace during the APCVD process. By tuning T_{gr} from 1000 to 1050°C and P_{CH_4} from 2 to 0.25 mbar, they decreased the nucleation site density from 60 to 2 nucl./mm². Vlassiouk *et al.* [81] investigated the role of the temperature in the 970-1080 °C range for both LP and AP CVD conditions. They observed that conducting the CVD growth at a temperature close to the melting point of copper was minimizing the domain density, regardless of the pressure regime. They also found that the high-temperature-induced C species desorption from the Cu surface occurs through the Cu evaporation at low pressure and through desorption of carbon clusters at ambient pressure conditions.

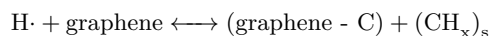
For both LP and AP CVD pressure regimes, it has thus been observed that relatively low CH_4 partial pressures and relatively high growth temperatures were key CVD conditions to reduce the nucleation site density and thus obtain larger graphene domains. For the nucleation site density, this observation is explained by the correlation between P_{CH_4} in the CVD atmosphere and the concentration of active C species present on the Cu surface. Lowering the gas phase concentration of methane leads to a reduction of the methane molecules dissociative breakdown rate on the Cu surface which thus decreases the supersaturation of C species required to initiate the nucleation [53]. The growth temperature dependency can be explained by considering the deposition rate and the mobility of C species present on the Cu surface. Performing the CVD process at high temperature improves the mobility of C species on the Cu surface and promotes their desorption from the Cu surface. High temperatures thus favors the attachment of C species on existing growing graphene islands over the formation of new graphene clusters with a supercritical size [53].

Maintaining a low partial pressure of methane is also essential to avoid the formation of additional layers [51,82,83]. These additional layers are believed to be induced by active C species that diffuse beneath the first growing layer without being attached on the first layer domain edges [84]. This phenomenon is more likely to happen when a relatively high active C species concentration is present on the Cu surface and when the adsorption rate of these species on the Cu surface exceeds the attachment rate on growing graphene domains.

Another sensitive parameter determining the nucleation site density is the hydrogen-to-methane ratio. Vlassiouk *et al.* [82] studied the contribution of hydrogen in the CVD growth of graphene at both LP and AP conditions. They observed that a certain amount of hydrogen in the CVD atmosphere was necessary in order to produce graphene. This result was attributed to the dissociation of molecular hydrogen from the atmosphere on the Cu catalyst to form active H $\cdot$ atoms in the Cu surface and bulk. These active H $\cdot$ atoms promote the adsorption of active C species on the Cu surface and thus act as co-catalyst for the graphene growth. These active H $\cdot$ atoms also promote the dehydrogenation of chemisorbed radicals (CH $_3$) $_s$ into (CH $_2$) $_s$, (CH) $_s$ and C $_s$. The complex graphene growth mechanism and the catalytic role of hydrogen are illustrated by the following reactions:



They also found that graphene domains grown under a low H $_2$ partial pressure were exhibiting a relatively irregular shape while those grown in the presence of a higher H $_2$ partial pressure were forming very regular hexagons with 120° corners. This phenomenon was assigned to the second role of H $_2$ that can act as a reagent that etches away the "weak" C-C bonds present on growing graphene domain edges. This effect is represented by the reaction:



The etching effect obtained when using a high H₂-to-CH₄ ratio is also believed to contribute reducing the nucleation site density [85].

The combined use of a high temperature [53, 54, 78, 80, 86], a low CH₄ partial pressure [78, 80, 87] and a high H₂-to-CH₄ ratio [54, 83, 85, 88] thus represent a key process requirement to be met in order to maintain a low density of graphene domains with a compact shape and minimal additional layers.

Cu foil *ex-situ* pretreatments

A major milestone toward the growth of large GDs consists in processing the Cu foils in order to remove the Cu surface morphology irregularities that have been shown to be preferential sites for nucleation, get rid of the Cu surface contamination and improve the catalyst purity [53, 89, 90]. In this regard, *ex-situ* Cu foil treatments including wet surface cleaning [91–94], mechanical/chemical/electrochemical surface polishing [53, 54, 92, 95], repeated growths [96] and Cu surface oxidation [87, 97], have been widely employed to improve the catalyst before loading it into the CVD furnace.

Cu foil *in-situ* pretreatments

In-situ treatments, including long-duration high-temperature annealing [54, 95, 98–101], substrate melting/re-solidifying [83], Cu surface recrystallization [98, 101] and Cu foil exposure to oxygen [102–104] taking place during the CVD protocol prior to the graphene growth step, have also been reported to reduce the nucleation site density. It appeared that introducing oxygen during the heating of the CVD furnace or just before initiating the graphene growth step is the most efficient approach to reduce the nucleation site density. This phenomenon will be discussed in more details in Chapter 6 and 7.

Customized Cu foil geometries

Beside fine-tuning the CVD parameters and processing the Cu foil, a few research groups employed more complex Cu foil geometries to further boost the size and compactness of growing GDs. These particular geometries – including either pockets/enclosures [88, 105, 106], stacks [107] and rolled-up [107] made of Cu foils – were argued to create enhanced growth conditions in the vicinity of the catalytic substrate compared to the mainstream conditions present in the CVD furnace. Chapter 4 provides a more comprehensive review of the various fundamental mechanisms that play a role in improving graphene growth when employing such Cu geometries.

Non-conventional CVD furnace configurations

Instead of carrying out the CVD process on a Cu foil lying flat on a horizontal support, the Cu foils have been placed into cuvettes [108–110] or restricted chambers [111, 112] when loaded inside the CVD reactor. These particular structures have been demonstrated to locally enhance CVD conditions near the Cu catalyst and thus improve the graphene results in a rather similar way as folding the Cu foils. More details about the impact of these furnace configurations are also provided in Chapter 4.

Presently, a few research groups achieved CVD-grown millimeter-size and more recently centimeter-size GDs on Cu foils. These results are summarized in table 2.1. This table provides information about the particular approaches employed, pressure regime, H_2 -to- CH_4 ratio and temperature. The graphene growth duration and graphene domain shape and maximum lateral size give an indication of the graphene growth rate and the growth behavior.

Table 2.1: Comparison of CVD parameters (growth pressure (P_{gr}) and temperature (T_{gr}), H_2 -to- CH_4 ratio), and graphene growth results (domain size, shape and edge morphology) obtained using Cu foils as catalytic substrates for the papers referenced in section 2.2.1.

References	Approach	P_{gr}	H_2/CH_4	T_{gr} [°C]	t_{gr}	Morphology	Max. size
Li <i>et al.</i> [78]	CVD cond. tuning	LP-CVD	$\sim 0.06-0.3$	1035	3min	Flowers	$\sim 25 \mu m$
Li <i>et al.</i> [105]	Cu Enclosure	LP-CVD	$\sim 1.5-4$	1035	$\geq 1h$	Dendritic	0.5 mm
Yan <i>et al.</i> [54]	In-situ anneal.	~ 144 mbar	~ 467	1077	7 h	Hexagonal compact	~ 4.5 mm
Wang <i>et al.</i> [99]	In-situ anneal.	Medium P-CVD	~ 1000	1045	15.5 min	Squared compact	$\sim 350 \mu m$
Zhang <i>et al.</i> [108]	Chuvette	LP-CVD	~ 12.5	1000	30 min	Dendrits	$\sim 100 \mu m$
Jia <i>et al.</i> [79]	CVD cond. tuning	LP-CVD	~ 6.7	1020	6 min	Dendrits	$\sim 100 \mu m$
Vlassiounk <i>et al.</i> [81]	CVD cond. tuning	AP/LP-CVD	~ 1800	1080	3 h	Hexagonal compact	$\sim 600 \mu m$
Zhou <i>et al.</i> [85]	pre-oxidation	LP-CVD	$\sim 1320-8800$	1070	48 h	Hexagonal compact	~ 5 mm
Gan <i>et al.</i> [113]	In-situ oxidation	AP-CVD	~ 2800	1050	$\geq 10h$	Hexagonal compact	~ 5.9 mm
Zhang <i>et al.</i> [80]	CVD cond. tuning	AP-CVD	$\sim 1000-8000$	1050	n/a	Round compact	~ 1 mm
Chen <i>et al.</i> [107]	Cu tube	LP-CVD	~ 7.2	1035	3-6 h	Dendritic compact	~ 2 mm
Hao <i>et al.</i> [102]	Cu passivation	LP-CVD	~ 20	1035	10-800 min	Dendritic compact	~ 1 cm
Mohsin <i>et al.</i> [83]	Resolidified Cu	AP-CVD	~ 2174	1075	300 min	Hexagonal compact	~ 1 mm
Eres <i>et al.</i> [87]	Pre-oxidized Cu	LP-CVD	~ 20	1040	2h	Dendritic compact	~ 1.5 mm
Wang <i>et al.</i> [110]	Chuvette /oxid.	LP-CVD	~ 500	1050	≤ 5 h	Hexagonal compact	~ 1.9 mm
Li <i>et al.</i> [104]	In-situ oxidation	AP-CVD	~ 6000	1075	4-20 h	Hexagonal compact	~ 1 cm
Song <i>et al.</i> [111]	Chuvette	LP-CVD	~ 125	1060	1 h	Dendritic compact	~ 1 mm
Chen <i>et al.</i> [112]	Restricted Chamber	LP-CVD	~ 22	1050	270 min	Dendritic compact	~ 0.8 mm
Miseikis <i>et al.</i> [106]	Ex-situ oxid. /Cu encl.	LP-CVD	~ 20	1060	3 h	Dendritic compact	~ 3.5 mm
Kraus <i>et al.</i> [103]	In-situ oxidation	LP-CVD	$\sim 250-1000$	950	30-60 min	Hexagonal compact	~ 1 mm
Wang <i>et al.</i> [114]	Oxidation /conf.	AP-CVD	~ 3500	1078	120 min	Hexagonal compact	~ 3 mm
Lin <i>et al.</i> [115]	Melamine treatment	LP-CVD	~ 5000	1020	≤ 36 h	Hexagonal compact	~ 1 cm
B.-Weimer <i>et al.</i> [90]	Ex-situ oxid. / polish.	50 mbar	~ 2889	1065	30	Hexagonal compact	~ 1 mm
Huet <i>et al.</i> [116]	In-situ annealing	800 mbar	~ 673	1050	2h	Hexagonal compact	~ 2.4 mm

2.2.2 Controlling the location of graphene domains

Although increasing graphene domain dimensions effectively contributes to reducing the density of GGB-induced defects, the random location of GGBs is particularly troublesome for fabricating electronic devices arrays and circuits at the industrial scale as they require a high device-to-device uniformity. For many practical applications, the fabrication of graphene devices does not require single-crystals larger than a few tens or hundreds of microns provided that these continuous defect-free graphene regions are aligned accordingly with the target circuit architecture. Pre-determining the location of nucleation sites represents a promising approach to ensure the fabrication of GGB-free devices while circumventing the need for the growth of giant graphene domains. The fabrication of complex circuits could thus be based on a series of well-organized individual single-crystals of graphene with moderate dimensions.

This strategy was first considered in 2011 by Yu *et al.* [117] that successfully produced a spatially ordered array of graphene single crystals. These crystals were grown from graphene seeds obtained by electron beam lithography patterning of a continuous graphene sheet that has been grown on the Cu substrate beforehand. Later that year, another research group also obtained a spatially ordered array of graphene single-crystals by locally depositing PMMA dots on the Cu foil surface. Upon the high temperature CVD process, these PMMA dots locally create a higher concentration of active C species that trigger graphene nucleation [118]. Very recently, similar results have been obtained by depositing chromium dots or printing carbon precursors onto the Cu foil surface prior to the graphene growth protocol [119,120].

Instead of pre-patterning seeds on the Cu substrate, Wu *et al.* [121] devised a method to locally induce the super-saturation of active C species in a single well-defined location on the Cu surface. This localized super-saturation has been achieved using a quartz nozzle that forces the precursor feeding into a small surface area of the catalytic substrate made of a Cu-Ni alloy to improve the growth rate. Thanks to this

method, they obtained an inch-scale single-crystalline graphene domain, which is the largest graphene domain produced to date.

Locally tuning the methane feeding on the Cu surface has also been exploited by Ding *et al.* [122] in order to control the location of graphene domains. In this case, the methane feeding is realized by a perforated Ni foil mask deposited on top of the Cu foil. The Ni foil is employed to regulate the local methane concentration in the atmosphere nearby the Cu foil surface. Graphene domains only grow if they are located sufficiently far away from the Ni foil that locally depletes the methane in its vicinity.

2.2.3 Controlling the lattice orientation of graphene domains

In contrast to the two approaches described previously that aim at avoiding the presence of GGBs in devices, this third strategy focuses on reducing the impact of grain boundaries on the graphene's physical properties. Murdock *et al.* [123] showed that under particular CVD conditions, there exists an epitaxial relationship between the growing GDs and the underlying Cu grain crystallographic orientation. Although the Cu substrate is polycrystalline, thermal treatments can be employed to increase the size of Cu grains and thus expand the surface area on top of which individual graphene domains will be aligned.

Aligned graphene domains have also been achieved by performing the CVD graphene process on melted Cu [124–126]. When heated up at 1160 °C under atmospheric pressure conditions, it has been observed that graphene domains are able to move on the liquid Cu surface and self-arrange into a perfectly-aligned uniform graphene array. Using melted Cu as substrate also has the advantage of producing graphene on a flat and smooth surface compared with polycrystalline Cu foils that exhibit cold-rolling-induced striations and grain boundary grooves.

Table 2.2: Comparison of CVD parameters (growth pressure (P_{gr}) and temperature (T_{gr}), H_2 -to- CH_4 ratio), and graphene growth results (domain size, shape and edge morphology) obtained using Cu foils as catalytic substrates for the papers referenced in sections 2.2.2 and 2.2.3.

References	Strategy	P_{gr}	H_2/CH_4	$T_{gr}[^\circ C]$	t_{gr}	Morphology	Max. size
Wu <i>et al.</i> [118]	PMMA seeds	APCVD	~ 1333	1050	20 min	Hexagonal compact	$\sim 25 \mu m$
Yu <i>et al.</i> [117]	Patterned seeds	APCVD	~ 4167	1050	10 min	Hexagonal compact	$\sim 16 \mu m$
Geng <i>et al.</i> [124]	Melted Cu	LP-CVD	~ 50	1120	38 min	Hexagonal compact	$\sim 150 \mu m$
Wu <i>et al.</i> [125]	Melted Cu	APCVD	~ 267	1090	15 min	Hexagonal compact	$\sim 200 \mu m$
Murdock <i>et al.</i> [123]	Cu orientation	LP-CVD	~ 100	1035	1 min	Hexagonal compact	$\sim 5 \mu m$
Wu <i>et al.</i> [121]	Quartz Nozzle	APCVD	~ 10000	1100	2.5h	Round compact	~ 1.5 inch
Ding <i>et al.</i> [122]	Perforated Ni foil	APCVD	~ 2000	1075	30-480 min	Hexagonal compact	~ 1 mm
Miseikis <i>et al.</i> [119]	Cr seeds	LP-CVD	~ 100	1060	30 min	Hexagonal compact	$\sim 350 \mu m$
Xu <i>et al.</i> [120]	Printed C dots	LP-CVD	~ 1250	1045	50 min	Hexagonal compact	$\sim 400 \mu m$

2.3 CVD of graphene on copper films

This section provides a detailed and up-to-date description of the various developments that have been achieved using thin Cu films instead of bulk Cu foils as catalyst for the CVD growth of graphene. The first growth of single-layer graphene on thin Cu film has been reported by Levendof *et al.* [127] in 2009. In that paper, they demonstrated that uniform transistor arrays could be directly fabricated after the CVD process on the synthesis substrate without any transfer process, thereby avoiding a series of issues related to the transfer technique.

Lee *et al.* [128] showed that using a rigid, flat and smooth substrate such as a thermally oxidized Si wafer could also be useful for improving the graphene transfer method. First, the growth substrate is compatible with standard CMOS technology techniques and can directly be processed prior to the transfer step. Second, the as-grown graphene sheet and the thin Cu film can be mechanically peeled from the substrate. As a consequence, the classical PMMA-assisted transfer process, which requires the Cu catalyst to be etched away, can be achieved more rapidly.

Cu thin films can also be employed to directly deposit graphene on various dielectric substrates using a single-step CVD process [129]. In this process, the Cu film is first employed as a catalytic substrate for the graphene growth and consecutively employed as a sacrificial layer which progressively sublimates during and after the high temperature graphene growth process. This method was shown to easily deposit a continuous graphene sheet with a surface area of about $20\text{ }\mu\text{m}^2$ on various substrates including thermally oxidized silicon, fused and single-crystalline quartz and sapphire wafers. In the same vein, it has been found that besides forming a graphene layer on top of the Cu film, adsorbed active C species are able to diffuse through the Cu film thickness (mainly through the Cu grain boundaries) and form graphene at the interface between the Cu film and the underlying SiO_2/Si substrate [130, 131]. This Cu-film-assisted CVD method can thus be used to directly deposit graphene on various substrates.

Issues related to the inter-diffusion between the Cu film and the underlying SiO₂/Si substrate have been first reported by Howsare *et al.* [132]. The instability of the Cu/SiO₂ interface during the high temperature CVD process leads to the formation of Cu-Si-O at the Cu top surface which adversely impacts graphene quality. Given the high temperature process, they showed that metallic (Ni, Cr, W) and dielectric (Si₃N₄, Al₂O₃, HfO₂) diffusion barriers were only having a limited effect on the stabilization of the interface.

Tao *et al.* [133] reported in a first paper that high-quality graphene could be obtained using a graphene growth step performed at low temperature (875 °C) and without hydrogen. They argued that in contrast to Cu foils, Cu films exhibit a predominant Cu(111) crystallographic orientation which can absorb a greater amount of hydrogen during the Cu annealing step and release it during the growth step. In a second paper, they claimed that the predominance of Cu(111) crystalline orientation is a key process parameter to grow a uniform graphene sheet with a quality comparable to exfoliated graphene over an entire 3-inch wafer [134].

All the aforementioned papers did not mention any graphene domain size or shape as they have been published before the graphene domain lateral size was considered as a figure of merit for graphene structural quality. In 2013, Jacobberger *et al.* [88] published a comprehensive study of the evolution of graphene domain shape and density as a function of the Cu surface orientation, global pressure and H₂-to-CH₄ ratio. Epitaxial Cu films with (100), (110) and (111) surface orientations have been obtained by Cu evaporation on crystalline MgO(100), MgO(110) and sapphire(0001) substrates, respectively. By enclosing Cu film pieces in a Cu foil pocket, they obtained graphene domains with a very dendritic shape and more compact square-shaped graphene domains with lateral dimensions reaching ~360 μm and ~125 μm, respectively.

In the ensuing years, a few papers reported the use of epitaxial Cu

film deposited on sapphire or spinel to grow compact hexagon-shaped graphene domains with a maximum lateral size of $\sim 200\text{ }\mu\text{m}$ [135–137]. To our knowledge, the largest graphene domains ever grown on thin Cu film reach a maximum lateral size of 1.6 mm [138]. The procedure employed to reach such a result is described in Chapter 6.

Table 2.3: Comparison of CVD parameters and graphene growth results obtained using Cu films as catalytic substrates.

Papers	Cu thickness	Annealing	P _{gr}	H ₂ /CH ₄	T _{gr} [°C]	t _{gr}	Max. size
Levendorf <i>et al.</i> [127]	500 nm	No anneal.	LP-CVD	~ 0.2	1000	20 min	n/a
Lee <i>et al.</i> [128]	700 nm	25 min, 1000 °C, H ₂	AP-CVD	~ 0.3	1000	~5 min	n/a
Ismach <i>et al.</i> [129]	100-450 nm	No anneal.	LP-CVD	~ 0.06	1000	15 min-7h	n/a
Su <i>et al.</i> [130]	300 nm	25 min, 750 °C, H ₂	LP-CVD	~ 0.2	900	~5 min	n/a
Kaplas <i>et al.</i> [131]	100-300 nm	No anneal.	LP-CVD	~ 1	950	n/a	n/a
Howsare <i>et al.</i> [132]	500 nm	30 min, 700 °C, H ₂	n/a	~ 0.2	1000	~10 min	n/a
Tao <i>et al.</i> [133]	0.5-1 µm	5 min, 875 °C, H ₂	n/a	~ 0	875-900	~5 min	n/a
Tao <i>et al.</i> [134]	1-1.5 µm	5 min, 975 °C, H ₂	n/a	~ 0	975	~5 min	n/a
Jacobberger <i>et al.</i> [88]	n/a	No anneal.	LP/AP-CVD	0.1-480	850-1050	n/a	360 µm
Lee <i>et al.</i> [139]	0.5-1.5 µm	240 min, 1000 °C, H ₂	LP-CVD	0.5	1000	45 min	~5-10 µm
Miller <i>et al.</i> [136]	450 nm	1h, 1050 °C, H ₂	LP-CVD	~ 0.8	1050	40 min	200 µm
Ago <i>et al.</i> [135]	500 nm	40 min, 1000 °C, H ₂	AP-CVD	~ 2200	1075	20 min	100 µm
Ago <i>et al.</i> [137]	500 nm	40 min, 1000 °C, H ₂	AP-CVD	~ 2200	900-1080	60-90 min	70 µm
Huet <i>et al.</i> [138]	1.2 µm	No anneal.	750 mbar	~ 700	1050	90 min	1.6 mm

2.4 Discussion: thin Cu films vs. Cu foils

Although a Cu film seems to be a more convenient platform for the realization of graphene-based practical applications and for the rigorous study of graphene growth mechanisms, the literature shows that Cu films are underexploited compared to Cu foils.

The key challenge for growing large GDs on Cu film lies in maintaining the Cu film's physical integrity upon the high temperature CVD process while using appropriate CVD conditions. Cu film degradation mainly arises from Cu evaporation loss [139], Cu film dewetting [129] or Cu interdiffusion with the underlying substrate [132]. Given that exposing the Cu film to high-temperature low-pressure conditions for an extended period of time severely damages the Cu film, the CVD protocol must be adapted.

Unfortunately, the CVD conditions that yield the best results in terms of graphene growth are also the ones that contribute the most to the Cu film degradation. Although this negative aspect is not directly and clearly emphasized in the literature, it can be readily observed by comparing tables 2.1 and 2.3. When growing graphene on thin Cu film, particular attentions have been directed to (i) shorten or avoid the Cu annealing step, (ii) decrease the growth temperature, (iii) shorten the graphene growth step, thus using moderate H_2 -to- CH_4 ratio to obtain a decent graphene growth rate and (iv) avoiding ultra-high vacuum or low pressure CVD processes.

These Cu film-induced limitations are clearly reflected in table 2.3. For instance, the growth temperature (T_{gr}) is usually kept below 1000 °C and the growth duration (t_{gr}) is shorter than 1 hour. The best results obtained on Cu films (aside from those achieved in this work) have been obtained on epitaxial Cu films that intrinsically exhibit a better adhesion to the underlying substrate and are less prone to suffer from voiding and dewetting. Moreover, these works have been achieved under ambient pressure conditions which reduces the Cu evaporation loss by about

3 orders of magnitude compared to LPCVD processes.

Unlike Cu films, Cu foils are more robust and can withstand harsher conditions including long Cu annealing step, graphene growth temperature close to the Cu melting point (regardless of the employed global pressure regime) and graphene growth durations exceeding a couple of hours (see table 2.1).

These considerations explain why many research groups demonstrated the growth of millimeter-size graphene domains on Cu foils while only the work carried out in the framework of this thesis accomplished such result on thin Cu films.

Chapter 3

Materials and Methods

This chapter describes the main equipment and materials that have been employed to study the synthesis of graphene. The first section describes the CVD equipment that has been initially operated to produce graphene. Section 3.2 presents the various available alternatives in terms of Cu substrates that have been used as catalytic surfaces for the chemical deposition of graphene. Section 3.3 then provides details on the graphene transfer procedure that has been widely employed during this research and how the method can be improved. Finally, section 3.4 describes the various characterization tools that have been used on a daily basis to assess graphene's domain size, structural quality and number of layers at the macro, micro and nanoscale.

3.1 Initial CVD equipment

The CVD equipment initially used in this research (illustrated in Fig. 3.1) was composed of the following elements:

1. **CVD furnace:** The CVD furnace is made up of a horizontal hot-wall CVD reactor (1.2 meter-long quartz tube with a 4-inch outer diameter) embedded in a double layer steel casing. The heated zone of the tube (~ 44 cm) is encased inside an alumina refractory sheath which contains the heating elements (Mo-doped Fe-Cr-Al Alloy). The furnace temperature is adjusted with a proportional-integral-derivative (PID) controller and a thermocouple (K-Type, Ni-Cr/Ni-Al, 220mm long, with ceramic sheath) which is in direct contact with the quartz tube. This system has been purchased in 2012 to MTI corporation.
2. **Gas feedstock:** The CVD furnace is supplied by 3 gas bottles purchased to Praxair: pure Ar (Research grade, 99.9999%), pure CH_4 (Research grade, 99.9999%) and an Ar/ H_2 gas mixture (5%).
3. **Mass flow controllers (MFCs):** The gas flow rates introduced in the CVD furnace are monitored and controlled using thermal mass flow controllers (Sevenstar, D07 series). These mass flow controllers feature various flow rate controlling ranges (also called "full scales", FS) and are usually calibrated using nitrogen (N_2). The actual gas flow rate injected can thus be calculated by multiplying the gas flow value displayed on the flow reader with the factor provided in Table 3.1.

Table 3.1: *Summary of full scales and calibration factors for the three MFCs connected to the CVD furnace.*

MFC	Full scale	Gas	Factor
1	100 sccm	CH_4	0.719
2	200 sccm	Ar/ H_2	1.32
3	500 sccm	Ar	1.415

4. **Pumping system:** The gas exhaust is achieved by a pumping system connected to the outlet of the CVD furnace. This system (HiCube 30 Eco) has been purchased to Pfeiffer Vacuum and is composed of a turbo-molecular pump (HiPace 30) and a dry (oil-free) diaphragm pump (MVP015-2 DC).
5. **Throttle valve:** The gas pressure inside the CVD system is coarsely controlled with a throttle valve placed between the CVD furnace outlet and the pumping system.
6. **Pressure gauge:** The global pressure present inside the CVD system is measured using a cold cathode/Pirani hybrid gauge (PKR251, Pfeiffer vacuum) which has been designed for vacuum measurement in the 5×10^{-9} -1000 mbar pressure range.

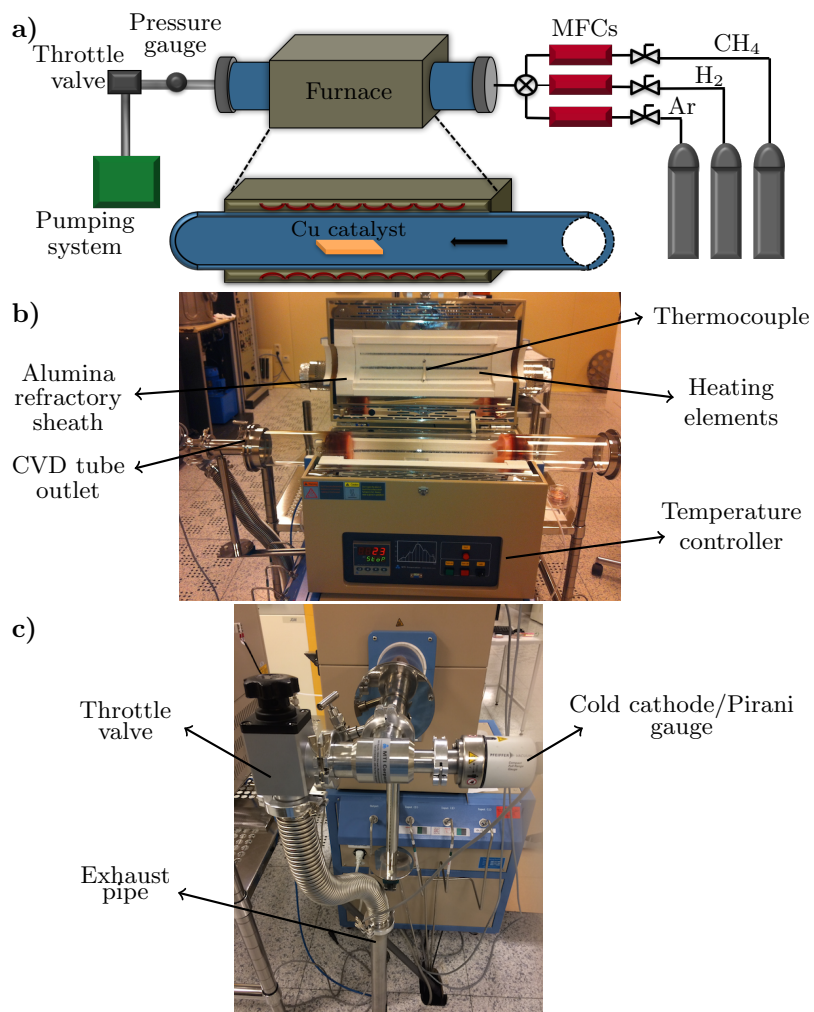


Figure 3.1: a) Schematic representation of the entire CVD system. b) Photograph of the CVD furnace (with the lid open). c) Photograph of the outlet of the CVD furnace with the pressure gauge, the throttle valve and the pipe going towards the pumping system.

3.2 Copper catalysts fabrication

The moderate catalytic activity and the low carbon solubility of Cu make it a perfect candidate for being used as a synthesis substrate for the chemical vapor deposition of graphene. In this thesis, two different types of copper catalysts have been studied: thin Cu films pre-deposited on 3-inch wafers and Cu foils.

3.2.1 Copper Foils

The Cu foils employed to grow graphene have been purchased to Advent Research Materials Ltd. They are available in a variety of thicknesses (ranging from 7 to 500 μm) and purities (ranging from 99.9% to 99.998%). In this thesis, the CVD experiments have been conducted using Cu foils with various thicknesses including 7, 25, 50 and 100 μm .

3.2.2 Thin Copper Films

The Cu films have been fabricated by electron beam evaporation of Cu pellets (Kurt J. Lesker Company, 99,999% pure) on various substrates:

1. **SiO₂/Si wafer:** Thermally oxidized Si wafers represent an attractive supporting material for the Cu film for different reasons: (i) silicon wafers are the standard in the semiconductor industry and are relatively cheap (Siegert Wafer Gmbh, ~ 275 euros/25 wafers), (ii) the silicon oxide quality and thickness can be easily tuned as it can be fabricated in the WINFAB¹ facility and, (iii) the SiO₂/Si can be used as a back gate which is convenient for directly fabricating field-effect devices on the synthesis substrate.

Unfortunately, it has been found that silicon is a strong contaminant for the CVD process and more particularly for the Cu catalyst

¹WINFAB, standing for Wallonia Infrastructure Nano FABrication, is a micro- and nano-fabrication platform consisting of a 1000 m² cleanroom on the site of Louvain-la-Neuve.

which is prone to form Cu-Si alloys under the high temperature conditions of the CVD process. It is thus critical to avoid the exposition of silicon to the CVD atmosphere (see Section 4.2). In order to address the Si-induced Cu catalyst poisoning, alternative supporting substrates have been explored.

2. **Fused quartz wafers:** Instead of using a Si wafer coated with a thin layer of SiO_2 , we purchased pure fused SiO_2 wafers (Prime Wafer, 3-inch diameter, $500\text{-}\mu\text{m}$ thick, surface roughness $R_a \leq 1.2$ nm, ~ 1500 euros/100 wafers). The chemical inertness, the high tolerance to high temperature operations (resistant to wide temperature gradients and high heat rates, softening point of ~ 1683 °C, thermal expansion coefficient of $\sim 5.5 \times 10^{-7}$ m/m at 300 °C), the high purity and the high cleanliness (compatible with semiconductor standard cleaning process) meet the high demands for the achievement of a repeatable, reproducible and successful CVD process.
3. **Sapphire wafers:** Sapphire substrates are single crystals of Al_2O_3 with a hexagonal crystalline structure and are usually available in C, R, A and M plane orientations. Sapphire wafers (Prime Wafer, 3-inch diameter, C-plane $\pm 0.5^\circ$ orientation, $430 \pm 15 \mu\text{m}$, epi polished, ~ 1450 euros/25 wafers) have also been purchased in order to control the texture of the polycrystalline Cu film, that is, the distribution of crystallographic orientations of Cu single-crystals (also called "grains"). As part of this thesis, C-plane orientation (0001) has been chosen in order to favor the development of the Cu(111) out-of-plane Cu film orientation. This epitaxial relationship comes from the fact that the Cu(111) surface has a hexagonal symmetry with a nearest-neighbor interatomic distance of 0.255 nm which matches with the hexagonal symmetry of C-plane sapphire which has an interatomic distance of about 0.238 nm (different from the lattice constants $a = 0.4763$ nm and $C \sim 1.3$ nm often referenced in the literature). In the most stable configuration, the Cu atoms are filling the octahedral interstitial sites in sapphire [140].

3.2.3 Intermediate Cu substrate results and discussion

Controlling the microstructure, texture and Cu substrate surface morphology is of central importance to achieve a graphene film with optimal physical properties. Increasing the copper grain size is essential in order to decrease the density of Cu grain boundary grooves that disturb the planarity of graphene and make it more prone to wrinkle once transferred. On the other hand, controlling the texture and more particularly harmonizing the Cu surface crystallographic orientation can contribute to reduce the misalignment between GDs. Better aligning GDs would potentially help reducing the detrimental effect of GGBs on the physical properties of the polycrystalline graphene sheet (as explained in subsection 2.2.3). Unlike Cu films that have their surface roughness mainly determined by the grain size and the depth of the grain boundary grooves, the Cu foils present a relatively rough surface characterized by periodic striations that are due to their cold-rolling-based manufacturing process.

Cu films

The modification of the Cu substrate texture and microstructure are mainly driven by the minimization of the surface, interface and internal strain energies and takes place through various diffusion processes [141]. In Cu films, these processes can thus occur during the Cu e-beam evaporation, after the deposition and/or during post-deposition annealings such as the chemical vapor deposition of graphene. During the Cu evaporation process, Cu vapor condenses on the substrate and forms small Cu islands. As the Cu deposition proceeds, these islands grow in three dimensions and eventually merge to form a continuous film. Any further supply of Cu contributes to the Cu film thickening and the formation of a columnar grain structure. This particular microstructure is caused by the fact that Cu atoms arriving on the growing film follow the crystallographic orientation of the grains (also called crystallites) they are attaching to.

In general, the microstructure and texture of as-deposited films are essentially controlled by the deposited material, the selected substrate and the deposition conditions. In the context of this thesis, the Cu film have been achieved using the e-beam evaporation equipment (Vacotec) present in the WINFAB platform which features a rather limited range of deposition conditions. It is found that the Cu deposition rate, which can be adjusted in theory in the 0.1-10 Å/s range², has little or no impact on the microstructure of the as-deposited Cu film.

Figures 3.2 and 3.3 show a 1.6 µm-thick Cu film as-deposited on fused quartz and crystalline sapphire, respectively. The columnar crystallite structure can be observed on the Cu film cross section once the Cu substrate is cleaved. Cu film surface images show that for both substrates, the size of the crystallites is the 40-100 nm range. The small crystallite size results from the relatively low temperature of the substrate during the evaporation process (near room temperature) which significantly limits thermally-activated processes and thus hinders the microstructure evolution. On the other hand, the crystallite's texture differs from one substrate to another as the Cu(111) orientation is epitaxially deposited on sapphire while the amorphous nature of the thermally oxidized silicon and fused quartz substrates does not yield a distinct texture.

For the growth of graphene, the Cu film microstructure and texture obtained just before the onset of graphene growth is of greater interest than those achieved right after the Cu film deposition process. The CVD protocol usually comprises a CVD furnace warming step and a Cu substrate annealing step prior to graphene growth. The high temperature employed during these steps promotes the diffusion of Cu atoms within the Cu film and causes a drastic modification of its microstructure and texture.

The photograph in Fig. 3.4 shows Cu films deposited on both fused quartz and crystalline sapphire substrates after a typical pre-CVD annealing process (consisting of a 1-hour-long heating step and 30-min-long

²Given that the CVD process requires a Cu film with a thickness exceeding 500 nm and given that overheating the crucible drastically reduces its life time, the deposition rate can be adjusted in the 2-5 Å/s range in practice.

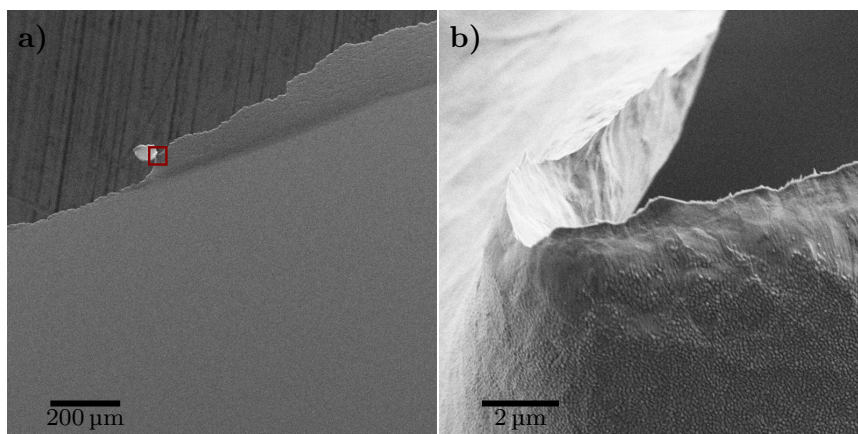


Figure 3.2: *E-T SEM images of a 1.6 μm-thick Cu film deposited on a fused quartz substrate. The Cu substrate has been cleaved in order to observe the Cu film cross-section. b) Higher magnification image of the surface area pointed out by the red rectangle in (a).*

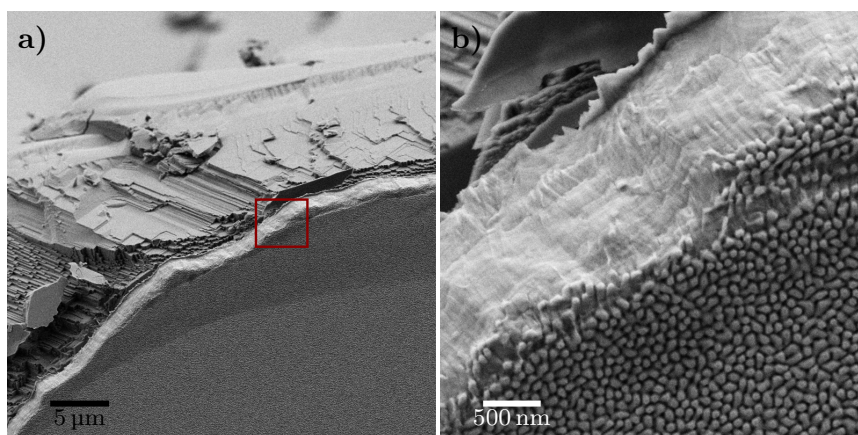


Figure 3.3: *E-T SEM images of a 1.6 μm-thick Cu film deposited on crystalline sapphire substrate. The Cu substrate has been cleaved in order to observe the Cu film cross-section. b) Higher magnification image of the surface area pointed out by the red rectangle in (a).*

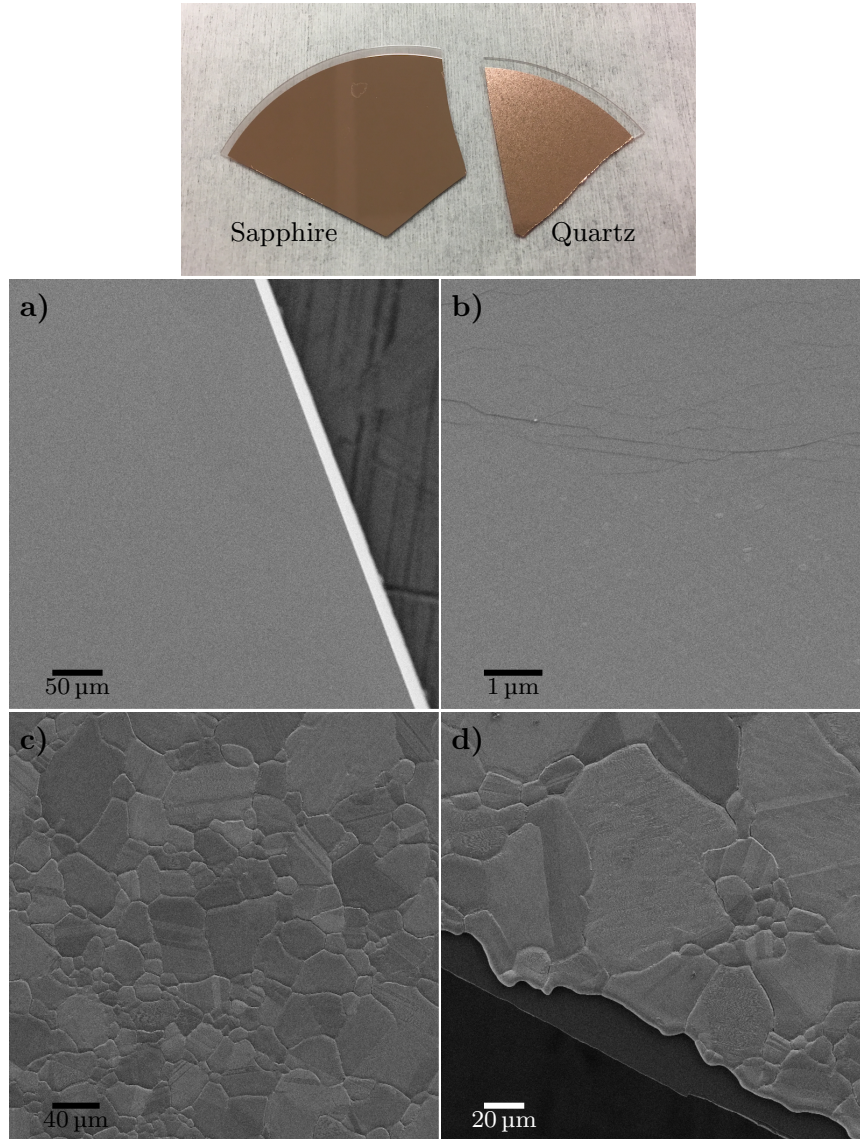


Figure 3.4: Comparison of the Cu film microstructure obtained upon annealing when it is deposited on a fused quartz and on a sapphire substrates. E-T SEM images obtained on the Cu film pre-deposited (a,b) on sapphire and (c-d) on fused quartz substrates.

annealing step at 1050°C). The difference in the reflectivity that can be observed with bare eyes arises from the marked Cu film surface morphology difference. Figures 3.4a and 3.4b show the ultra smooth grain-boundary-groove-free Cu surface obtained using sapphire as a substrate. Given that the film has been epitaxially deposited on the sapphire substrate, all Cu crystallites have the same out of place orientation and can seamlessly merge together to become what seems to be a 3-inch single-crystalline Cu film. In contrast, annealing the Cu film deposited on the fused quartz material causes the crystallites to grow and become Cu grains that expand through the entire Cu film thickness (see Fig. 3.4d) and over a few tens or hundreds of micrometers in the Cu film plane.

The ~ 2000 -fold improvement of the Cu grain size achieved upon the thermal treatment evidences that the pre-growth Cu annealing has a far greater impact on the microstructure and texture compared with the conditions of Cu film deposition. As a consequence, it is rather pointless trying to fine-tune the deposition parameters such as the deposition rate. It seems rather evident that customizing the e-beam evaporation equipment in order to maintain the substrate at a certain temperature (higher than room temperature) during the deposition process would have had a negligible impact compared with the temperature achieved during the CVD which is very close to the melting point of copper ($T_m=1084^\circ\text{C}$).

Cu foils

Compared to thin Cu films, as-received Cu foils exhibit a strong surface morphology originating from their fabrication process. Striations with rather similar depths and widths are observed on Cu foils regardless of their thickness as shown on the optical pictures and the profilometer scans in Fig. 3.5.

In the case of Cu foils, the microstructure and texture are predominately dictated by the pre-growth thermal treatment. The size of Cu grains essentially depends on the Cu foil thickness, the annealing temperature, the annealing duration and the purity of the Cu foil. Exposing the Cu foils to high temperature ($T\sim 1050^\circ\text{C}$) for about one hour leads to the

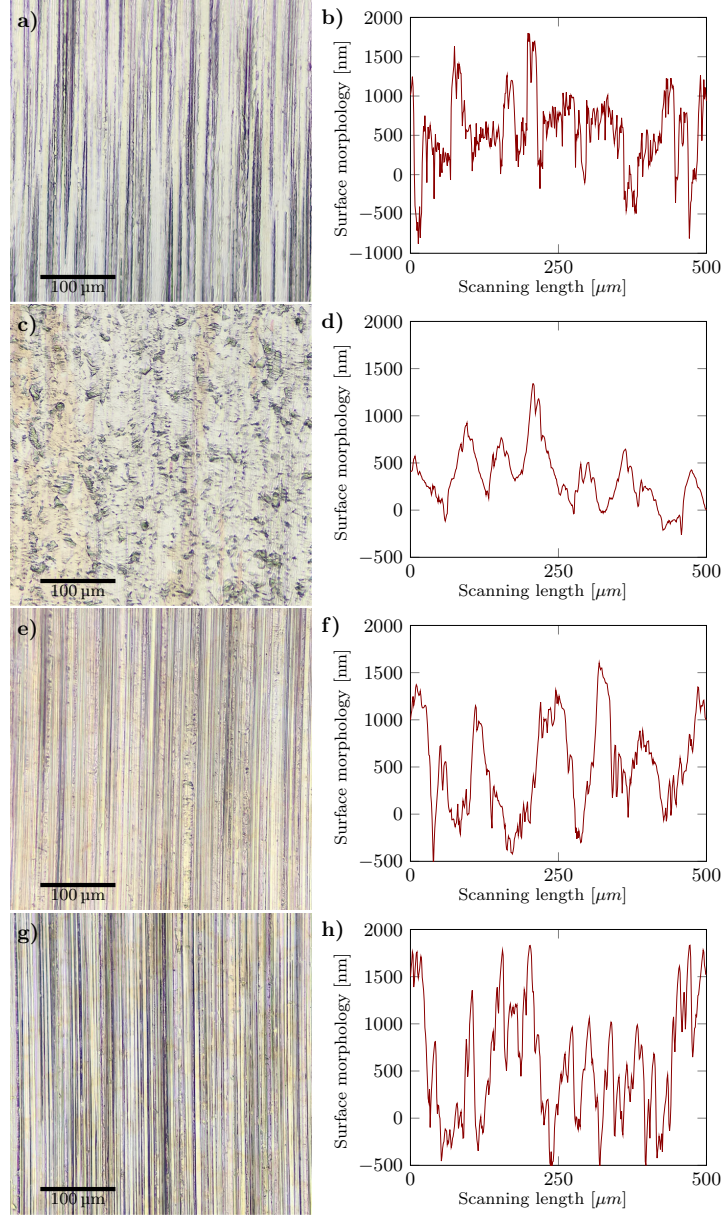


Figure 3.5: Optical microscopy images (left panel) and surface morphology profiles (right panel) taken on the surface of as-received Cu foils with thicknesses of (a-b) 7 μm , (c-d) 25 μm , (e-f) 50 μm and (g-h) 100 μm . Profilometer parameter: stylus tip radius: 2.5 μm , scanning length: 500 μm and vertical force: 3 mg

formation of Cu grains that extend over the entire Cu foil thickness and a few millimeters in the Cu foil plane as shown in Fig. 3.6. Due to the high temperature thermal treatment, the Cu foil softens and conforms with the surface on which it is deposited (a ceramic boat or some pieces of quartz-made glassware). When the Cu surface stays in close contact with the second material for a relatively long time, the Cu foil locally melts and sticks to the supporting material. For moderate exposure durations to high temperature (≤ 80 min at $T \leq 1050^\circ\text{C}$), this softening and sticking phenomenon is quasi inexistent for 50- and 100- μm -thick Cu foils while it prevents the use of 7- μm -thick Cu foils that are more delicate and prone to tear at the grain boundary grooves as shown in Fig. 3.6a.

As a consequence, the 25- and 50- μm -thick Cu foils have been preferred over the 7- μm -thick one for the CVD experiments conducted in this thesis (see Chapter 7). The 100- μm -thick Cu foils have not been used very often for a few reasons. First, the greater amount of Cu material makes these Cu foils more expensive than thinner foils. Second, the transfer step of graphene requires the Cu foil to be completely etched away in a Cu etching solution. Using a thicker Cu foil thus makes that process step more time and resource consuming. In a more scientific point of view, thicker Cu foils can store a larger amount of carbon and oxygen atoms that play a role in graphene growth. Therefore, minimizing the thickness makes the CVD growth process more controllable. Finally, the high-temperature of the CVD process causes the Cu foils to soften and conform to the underlying substrate, thereby reducing the gap separating the foil from its supporting substrate. Reducing this gap is beneficial to reduce the growth of parasitic multilayer graphene regions (see Chapter 7). It is thus more interesting to have Cu foils with thicknesses comprised between 25 and 50 micrometers that better conforms to the underlying substrate upon the high temperature treatment.

On the other hand, the texture also strongly varies upon the thermal treatment. Given the high temperature CVD process ($T_{\text{gr}} \geq 1000^\circ\text{C}$) which is close to the Cu melting point, the excess of strain energy ori-

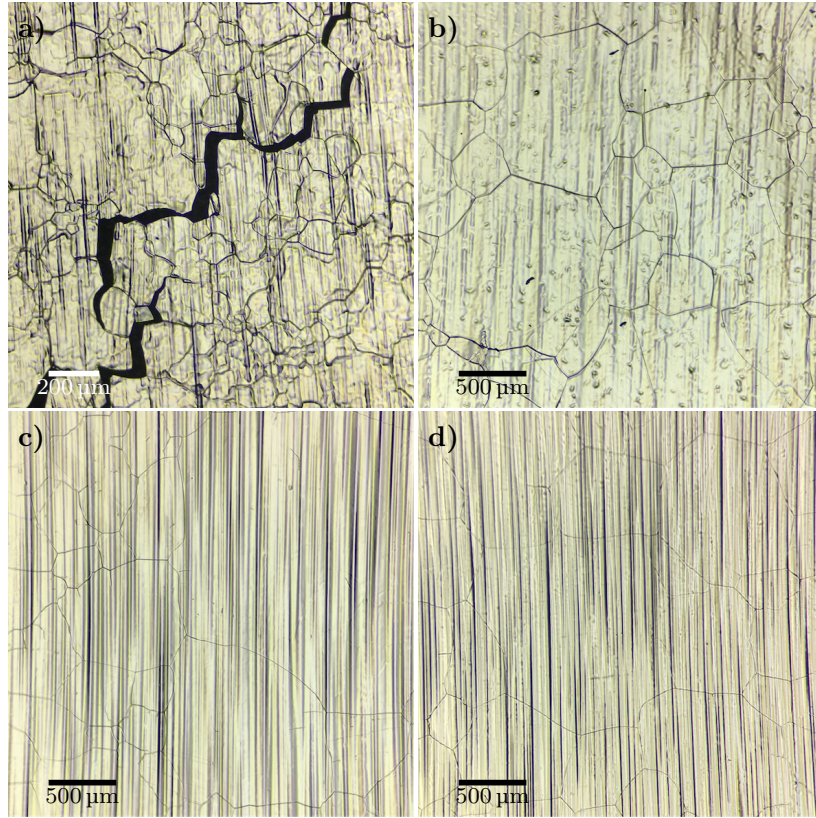


Figure 3.6: Optical microscope images of Cu foil surfaces after a typical Cu annealing process (1-h-long heating step and a 30-min-long plateau at 1050°C). Images in (a), (b), (c), and (d) correspond to Cu foils with thicknesses of 7, 25, 50 and 100 μm, respectively

ginally present in the as-received Cu foil or engendered during the heating ramp vanishes. Hence, the excess of strain-related energy does not contribute to the microstructure/texture evolution. Therefore, the main driving force concerns the minimization of energy of the free surfaces of the grains, that is the energy corresponding to the Cu grain surfaces at the Cu foil topside and backside. As the surface energy density of (111) texture is inferior to those of (110) and (110) textures, it is expected that Cu(111) grains will develop at the expense of other Cu grains with other orientations [142].

As explained in the literature review in chapter 2, the Cu foils can be prepared ex-situ in order to address the Cu surface morphology issues. The Cu foil rolling striations are most often suppressed using a chemical/mechanical polishing method which consists of two successive steps: the diamond polishing (DP) and the oxide polishing (OP). DP employs small diamond grains as an abrasive which, due to their hardness, cut extremely well through all materials and phases and thus leads to fast and efficient material removal. These diamond grains however tend to produce fine scratches in soft and ductile materials such as copper. These scratches are removed using a colloidal suspension of silica with a pH of about 9.8 which provides both a chemical action and fine and gentle mechanical abrasion. In practice, the DP (MD-mol surface, DiaPro Mol R3, 3- μm -large diamonds, 150 rpm, 2 min) and OP (MD-Chem surface, OP-S NonDry, 0.04- μm -large silica grains, 150 rpm, 2 min) steps have been achieved using Struers materials and procedures. This procedure greatly improves the surface morphology as shown in Fig. 3.7a. Although very fine scratches are still present on the Cu surface, they vanish after a one-hour-long Cu annealing step at 1050 °C and near ambient pressure conditions as shown in Fig. 3.7b.

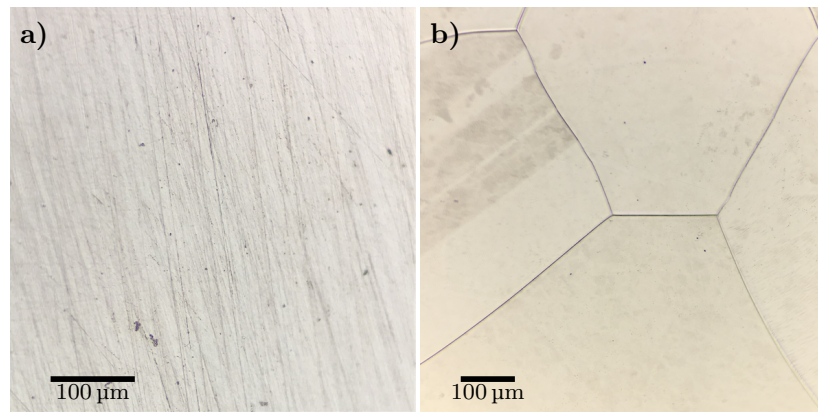


Figure 3.7: *Optical images of Cu surface after an ex-situ chemical/mechanical polishing process (a) before and (b) after a typical high temperature Cu annealing step.*

3.3 PMMA-assisted transfer of graphene

The industrial production of graphene-based devices requires the development of a large-scale high-quality graphene synthesis technique in conjunction with a reliable and scalable transfer method. This transfer step is required to separate graphene from its synthesis substrate and move it onto a device-compatible substrate (typically an insulator). It is crucial for device performance, yield and uniformity that graphene's physical properties are not degraded upon the transfer process.

Besides the scotch tape transfer initially used for the micro-mechanical exfoliation of graphite, the first transfer process has been demonstrated in 2008 by Reina *et al.* [143] who successfully transferred exfoliated graphene flakes pre-deposited on a SiO₂/Si substrate onto a second SiO₂/Si substrate or poly(dimethylsiloxane) (PDMS). Their method was based on the spin-coating of a thin PMMA film on the first SiO₂ surface containing the graphene flakes, the wet etching of the SiO₂ layer in a NaOH solution, the transfer of PMMA/graphene film onto the target substrate and the PMMA removal using acetone.

It did not take long before the first demonstration of the transfer of CVD-grown graphene. Soo Kim *et al.* [144] transferred graphene grown on a thin Ni film substrate onto a SiO₂/Si substrate using a PDMS stamp that has been cured directly on the graphene film. Since then, the scientific community has generated extensive literature and practice on transferring graphene onto various device-compatible substrates. Most of the techniques reported so far proceed as follows: a temporary supporting layer is deposited on graphene to improve its mechanical stability, the graphene/support stack is then separated from the synthesis substrate and gently deposited on the target substrate where the supporting layer is finally removed. These techniques however differ by (i) the origin of graphene (exfoliated from graphite, CVD on metals, growth on SiC), (ii) the nature of the supporting layer (scotch tape, PMMA, PDMS, metal film, thermal release tape, polycarbonate, h-BN), (iii) the graphene initial substrate removal approach (mechanical peeling, wet

etching, electrochemical delamination or etching, wet delamination), (iv) the graphene deposition approach (wet scooping, elastomer stamp, roll-to-roll/stamp, hot pressing), (v) the supporting layer removal, and (vi) additional intermediate steps.

3.3.1 Transfer procedure

Although numerous techniques have been developed, the scientific community did not reach a common agreement on a specific transfer procedure which is scalable, clean and maintains the structural integrity of graphene. In the framework of this thesis, CVD-grown graphene has been routinely transferred from the Cu foil or film onto a SiO_2/Si substrate using the classic PMMA-assisted wet transfer method described in Fig. 3.8.

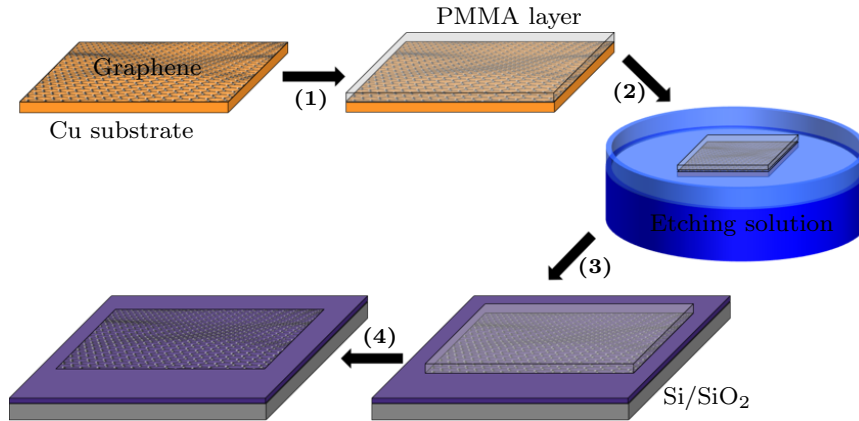


Figure 3.8: General process flow for the PMMA-assisted transfer procedure: (1) PMMA spin-coating directly on the graphene/Cu substrate, (2) Cu removal in a Cu etching solution and graphene rinsing with de-ionized water, (3) graphene/PMMA scooping with the SiO_2/Si substrate and, (4) PMMA removal with acetone.

Although this method has major disadvantages for the realization of high performance electronics (see subsection 3.3.2), this method is suitable for graphene characterization purposes in the sense that it allows the rapid transfer of large surface areas. The detailed procedure consists of the following steps:

- 1. PMMA spin-coating:** PMMA (950 PMMA A9, MicroChem) diluted in anisole (99%, Sigma-Aldrich) is directly spin-coated on the graphene for one minute. Depending on the rotation speed and the dilution of PMMA, various thicknesses can be obtained varying from ~ 60 nm to ~ 2100 nm with 6000 rpm of 2% PMMA and 1000 rpm of 9% PMMA, respectively. In the case of graphene grown on Cu foils, the graphene sample is placed on a rigid and flat support (i.e. a dummy Si wafer) in order to ensure the deposition of a uniform PMMA layer. Unfortunately, the liquid PMMA tends to penetrate underneath the Cu foil and propagate at the interface between the Cu foil backside and the support, which is very undesired given that the Cu foil has to be etched away afterwards in the Cu etchant. To avoid this phenomenon, the Cu foil is carefully attached using Kapton tape on the sample edges, thus making the Cu foil backside hermetically sealed. Also in the case of Cu foils, the PMMA/Gr/Cu stack is detached from the support, flipped and re-attached hermetically on it (using Kapton tape) in order to etch graphene grown on the Cu foil backside using an oxygen plasma. Protecting the topside from the oxygen plasma is essential to avoid the degradation of PMMA layer including its thinning that would make it more fragile or its reticulation that would make the PMMA layer more difficult to remove at the end of the transfer process. Etching the graphene on the Cu foil backside is crucial in order to have a uniform and rapid Cu etching and avoid the redeposition of agglomerated graphene fragments on the bottom side of the floating graphene/PMMA film once the Cu is etched away.
- 2. Cu substrate etching and graphene rinsing:** The sample is deposited on the surface of a Cu etchant bath consisting of either ac-

tivated FeCl_3 (C.I.F), Ammonium persulfate (APS) (Merck, Millipore Corp, extra pure) or a commercial Cu etchant (Cu etchant 49-1, electronic grade, Transene inc.) based on citric acid ($\text{pH}=5.9-6.5$). Once the Cu substrate is totally etched away, the etching solution is gently and gradually replaced by de-ionized water in order to rinse graphene.

- 3. Graphene/PMMA scooping:** The graphene/PMMA stack floating on the de-ionized water is scooped by the target substrate and let to dry.
- 4. PMMA removal:** The PMMA layer is then removed using a warm acetone bath (50°C) for at least 1 hour. The bath is then naturally cooled down to room temperature before successively rinsing the sample with fresh clean acetone, isopropanol, methanol and water. If necessary, PMMA residues can be removed using PG remover (MicroChem) or diluted acetic acid.

3.3.2 Transfer-related challenges

There are four major areas of concern when considering the development of an efficient transfer method and the fabrication of high performance graphene-based devices:

- 1. Contamination** Performance of graphene electronic devices is often reduced by contaminants introduced during the transfer process steps. These contaminants, trapped in direct contact with carbon atoms composing the single-layer graphene, act as extrinsic scattering centers and reduce carrier transport properties. Two different kinds of residues can be induced during the transfer process:
 - **Polymer residues:** The exposure of graphene to polymeric supporting materials inevitably contaminates the graphene surface with residues which are not easy to remove with standard solvents due to their strong van der Waals interactions.

- **Metallic particles:** Wet etching of metal substrate also contributes to graphene contamination through oxidized metal particles which are not easily washed off.

- 2. Physical integrity** Single-layer graphene is prone to ripping, tearing and folding. Cracks and tears into the graphene film decrease device yields and weaken graphene-based suspended structures. A supporting layer is often used to facilitate the handling of the single-layer graphene during the delicate and cumbersome process steps. However, using a supporting layer involves additional process steps that may introduce defects.
- 3. Chemical purity** Wet chemical processes are often used to get rid of the growth substrate or the supporting layers. Etching solutions can react with graphene and functionalize its surface by adding oxygen-based compound (hydroxyl, carbonyl, epoxy). Choosing chemicals that cannot create new covalent bonds with carbon atoms is critical to maintain graphene's excellent physical properties.
- 4. Mechanical stress** Cu substrate surface is not atomically smooth, especially after the synthesis substrate microstructure evolution taking place upon the high temperature CVD process. Graphene growth follows the rough Cu surface and mimics its morphology. Transferring this non-planar graphene sheet onto a smooth rigid and flat surface is very likely to result in local stress and wrinkles in the graphene sheet.

In this context, the wet PMMA-assisted method is not very convenient for the realization of electronic devices with optimal performances as it results in PMMA residues, water molecules trapped at the graphene/SiO₂ interface along with remainders of Cu and Cu etchant. Moreover, the physical integrity of the transferred graphene film significantly depends on the operator's dexterity. The transfer process deleterious impact can however be mitigated by adapting the procedure and using a few tricks.

First, PMMA residues can be reduced by avoiding any baking steps. Although the PMMA is often baked (at about 120 °C for a few minutes)

in order to get rid of residual solvents (anisole) after the spin coating, it is preferred to let the PMMA layer dry under ambient air at room temperature overnight. Baking the PMMA makes it stick more to graphene and thus makes it more difficult to remove. In the same vein, heating the Cu/graphene sample (prior to PMMA deposition) in order to make graphene domain visible also makes PMMA more difficult to remove after the transfer process. Figure 3.9 shows that PMMA has a better adhesion with graphene than SiO_2 when the Cu foil has been baked (200°C for 3 min) prior to the transfer process and when the PMMA is baked on a heating plate for 5 min at 120°C . It is also essential to avoid the exposure of the PMMA layer to the O_2 plasma employed to etch the graphene on the Cu foil backside as it also makes the PMMA more resistant to solvents.

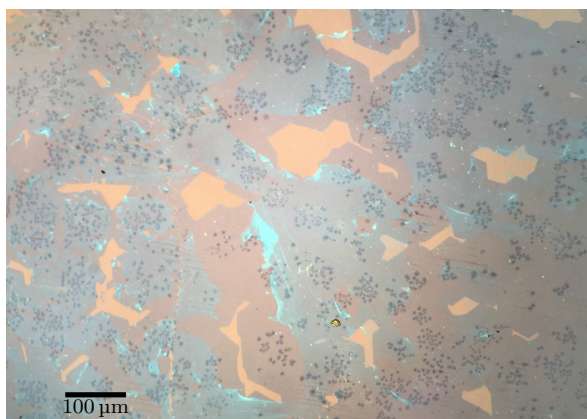


Figure 3.9: *Optical microscope image of CVD graphene transferred onto a SiO_2/Si substrate using baked PMMA as supporting layer.*

The contamination resulting from the Cu removal step can be also reduced by conducting a proper rinsing. In order to limit the consumption of FeCl_3 , the Cu etching is achieved using a watch glass dish as shown in Fig. 3.10a. Once the Cu substrate etching is completed (see Fig. 3.10b), de-ionized (DI) water is gently added to the bath to start the rinsing process. Given that the Cu etchant and Cu ions are heavier than water, gently pouring water results in a heterogenous mixture as shown in Fig.

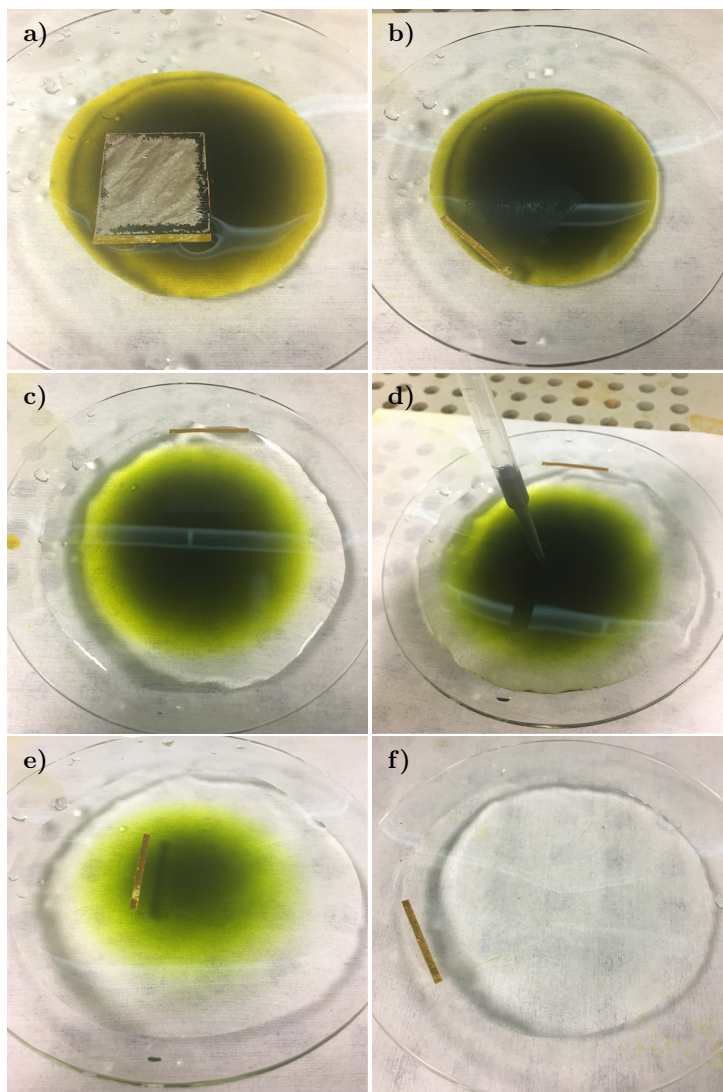


Figure 3.10: Photographs showing the various sub-steps involved in the Graphene/PMMA film rinsing procedure. a-b) the Cu foil is etched away for about 30 min (for a 25- μm -thick foil). The rinsing proceeds by (c) gently adding DI water to the bath while (d) withdrawing the by-product of the Cu etching reaction from the watch glass bottom where it concentrates. Repeating this procedure leads to a colorless bath (f).

3.10c. Owing to the particular geometry of the watch glass, the concentrated FeCl_3 and Cu etching by-products can be directly collected from the bottom of the glass watch using a pipette (see Fig. 3.10d). After a few successive DI water additions and FeCl_3 withdrawals, a clear solution is obtained. Although this solution is colorless, directly scooping the PMMA/graphene layer would result in a strong contamination and a poor adhesion of graphene on the target substrate. In order to obtain a better rinsing, the small volume of the dish along with the floating graphene/PMMA film is poured into a 2-liter glassware tank. After 30 min, the watch glass dish is used to scoop the graphene/PMMA film and transport it into a second 2-liter glassware tank. After repeating this step at least 3 times, the cleanliness of the graphene is greatly improved.

The density of wrinkles and most likely the strain of graphene can be reduced by making the SiO_2 surface more hydrophilic. Using an O_2 plasma or immersing the SiO_2 in a warm Piranha bath ($\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$) for a couple of minutes as pre-treatment helps the graphene/PMMA film spreading on the SiO_2 surface after the scooping process step. In contrast, having a hydrophobic SiO_2 makes the graphene/PMMA film pilling up on itself because the contact angle of the water trapped between the graphene and SiO_2 makes the PMMA/graphene film spread over a SiO_2 surface area smaller than its actual surface area as shown in Fig. 3.11.

As the drying proceeds, the water flows along the graphene/ SiO_2 interface towards the sample edges and the capillarity forces gradually pull the film made of PMMA and graphene down in close contact with the underlying SiO_2 surface. The excess of PMMA/graphene film surface area turns into transfer-induced wrinkles as shown in Fig. 3.11. The macro-scale wrinkles observable with bare eyes in Fig. 3.11a-b turn into very thin wrinkles as visible with the optical microscope in Fig. 3.11f. Making the SiO_2 hydrophilic contributes to reducing the phenomenon.

The physical integrity of graphene strongly depends on how the thin PMMA/graphene film is handled once the Cu foil or film is etched away.

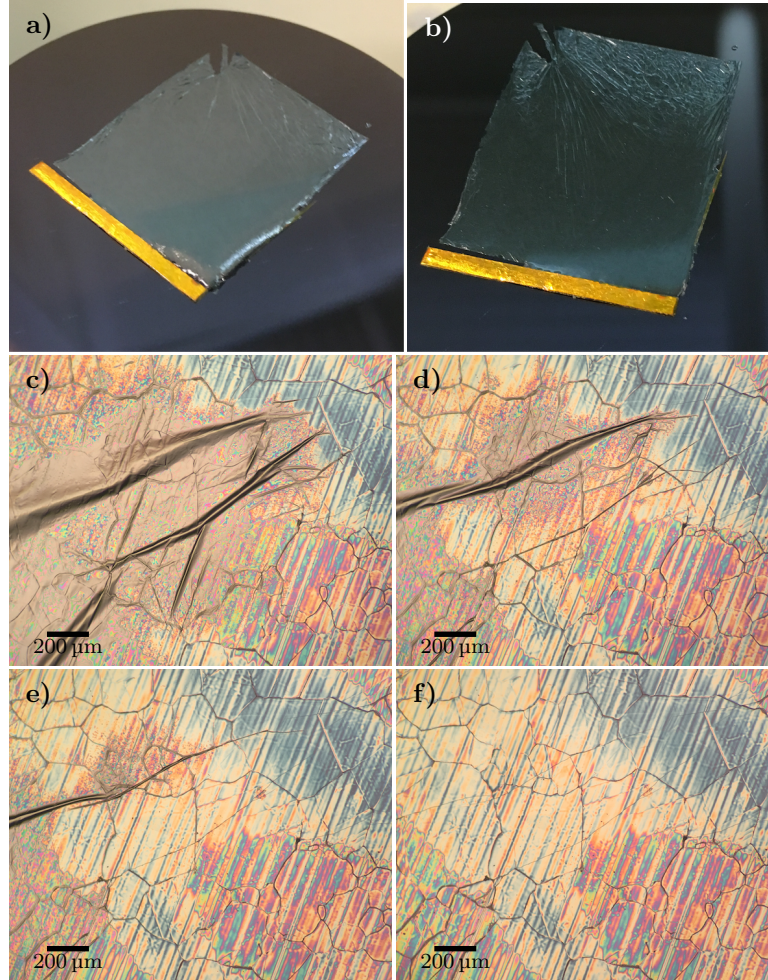


Figure 3.11: *a-b) Photographs of the PMMA/graphene film on a SiO₂/Si wafer after the scooping transfer step. c-f) Optical microscope images of the PMMA/graphene film deposited on the SiO₂/Si wafer right after the scooping transfer step. Images (c) through (f) show the evolution of the drying process with time at the exact same location.*

Using a thick PMMA layer makes the PMMA/graphene film more robust upon the rinsing and scooping steps. Because the graphene and PMMA are strongly coupled, the graphene cannot be severely damaged during the rinsing and scooping steps as long as the PMMA film remains intact and does not undergo any important strain.

It has however been observed that using a thick PMMA layer does not help maintain the physical integrity of graphene. This observation stems from the fact that the most sensitive step contributing to major damages in graphene is the PMMA removal step. More particularly, the main factor responsible for the deterioration of the physical integrity of graphene is its adhesion on the target substrate.

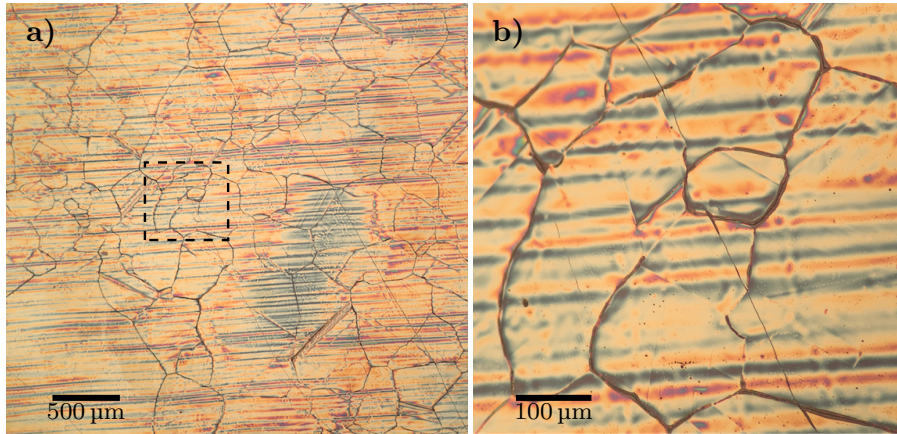


Figure 3.12: *Optical microscope images of the PMMA/graphene film deposited on the SiO_2/Si wafer right after the scooping transfer step. Images (b) shows a higher magnification of the surface areas pointed out by the dashed square in (a).*

When the PMMA layer is deposited on the graphene/Cu substrate, it conforms to the underlying surface and mimics the Cu/graphene surface morphology. Once the anisole has evaporated, the PMMA layer forms a relatively rigid mold of the grain boundary grooves and cold-rolling striations. Even after Cu substrate etching and PMMA/graphene film

scooping, the film still has the Cu surface morphology footprint as shown in Fig. 3.12.

The color contrast observed on the optical images reflects a variable spacing between the graphene/PMMA film and the underlying surface due to the strong surface morphology. As the adhesion of graphene on the SiO₂ is only achieved through van der Waals forces, it is of central importance to ensure the proper contact in order to reach a strong adhesion. The graphene surface areas that are not in close contact with the SiO₂ surface are washed away upon the PMMA removal step as acetone will intercalate underneath graphene.

Cracks, tears and folds in graphene can thus be mostly prevented by improving the contact. One first approach consists of heating the PMMA layer above its glass transition temperature ($\sim 104^\circ\text{C}$) for about 30 min so that the PMMA/graphene layer softens and better conforms to the underlying substrate [145]. Although this approach helps maintaining the physical integrity of graphene, it makes the PMMA removal more difficult as the PMMA has been baked. A better approach consists of gently softening the PMMA film by re-depositing fresh PMMA on top of the PMMA/graphene film [146]. Although they re-cure the PMMA after its re-deposition in their paper, it is found here that leaving a thick fresh PMMA layer for 30 min and then directly proceeding to the PMMA removal greatly improves the graphene cleanliness.

The rather uniform contrast in Fig. 3.13 demonstrates the suppression of the spacing between graphene and the SiO₂ surface after the fresh PMMA re-deposition. It has also been observed that initially spin-coating a thin PMMA layer (~ 100 nm) gives better results as the thickness is thick enough to go through the different process steps without major damage while being thin enough to easily soften and conform to the underlying surface.

Figure 3.14 shows a continuous single-layer graphene sheet (grown on a Cu film) after its transfer onto a 300-nm-thick SiO₂/Si substrate. Directly removing the PMMA film without re-depositing the fresh PMMA

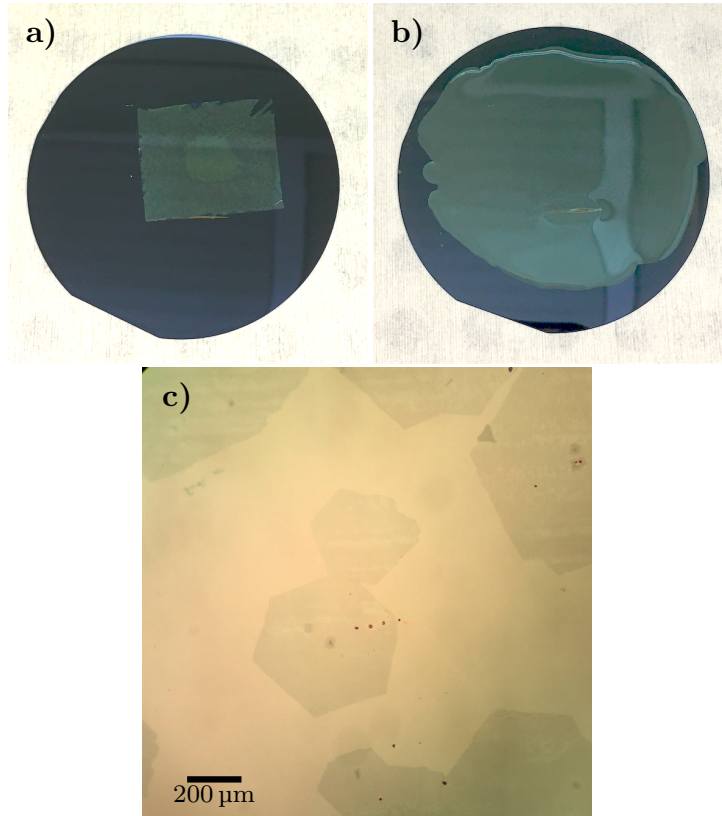


Figure 3.13: *a-b) Photographs of the PMMA/graphene film deposited on SiO_2/Si wafer (a) before and (b) after the re-deposition of fresh PMMA. c) Optical microscope image of the PMMA/graphene film after the re-deposition of fresh PMMA (before it fully dried).*

results in severe degradation of the graphene's physical integrity (see Fig. 3.14a). The small patches of continuous graphene that are deposited on the SiO_2 surface correspond to graphene areas that were present on top of Cu grains while the cracks and folds mainly correspond to graphene areas that were localized in or near Cu grain boundary grooves. The Cu grain boundary grooves imprinted in the PMMA/graphene reduce the adhesion of graphene with the underlying substrate and make it

more prone to tearing and folding upon the PMMA removal step. Re-depositing fresh PMMA helps improving the contact of graphene with the SiO_2 surface and yields better transfer results as shown in Fig. 3.14.

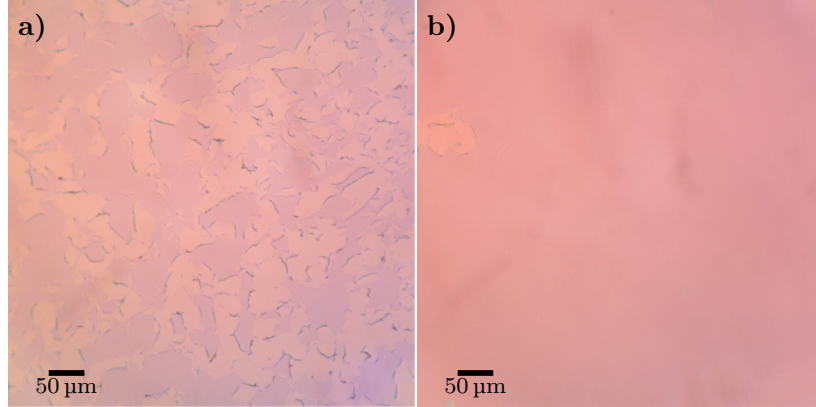


Figure 3.14: *Photographs of a continuous graphene film deposited onto a 300-nm-thick SiO_2/Si substrate. The transfer procedure has been achieved (a) without or (b) with the fresh PMMA re-deposition step.*

3.3.3 Conclusions

Although the PMMA-assisted transfer process is far from being suitable for the realization of high-performance graphene based devices, it represents a relatively easy, rapid and reliable method to transfer graphene films of several square centimeters. Knowing which transfer process steps are responsible for the formation of wrinkles, cracks or contaminations is critical in order to further improve the procedure.

3.4 Graphene characterization techniques

Characterizing graphene throughout the various research and development activities that eventually lead to the fabrication of graphene-based practical applications is crucial for achieving good performances. This section aims to describe the various tools that have been used in order to assess graphene's continuity, physical integrity, number of layers and structural quality.

3.4.1 Optical microscopy

Although graphene is an atomically thin material and absorbs only 2.3% of the white light, graphene can be observed with an optical microscope or even with bare eyes under certain circumstances.

Direct observation on the catalytic substrate

As graphene is quasi-transparent, it is challenging to directly observe it on its synthesis substrate using a classical optical microscope. However, a Cu surface covered by graphene usually features atomically flat planes, facets, step edges and vertices which contrast with bare Cu which exhibits a smoother surface as shown in Fig. 3.15. It is still unclear whether this contrast is linked to the presence of graphene during the high-temperature CVD process which causes a slight modification of the Cu surface morphology or if it is simply due to the fact that graphene prevents the Cu surface to rapidly grow a native oxide that smoothens the surface once the sample is unloaded from the furnace and exposed to ambient atmosphere.

As the contrast is very weak, this visualization technique can only be used when observing isolated graphene domains (i.e. when the graphene film is not complete). Although this technique is non-destructive and straightforward, it falls short of assessing the number of layers or the structural quality of graphene.

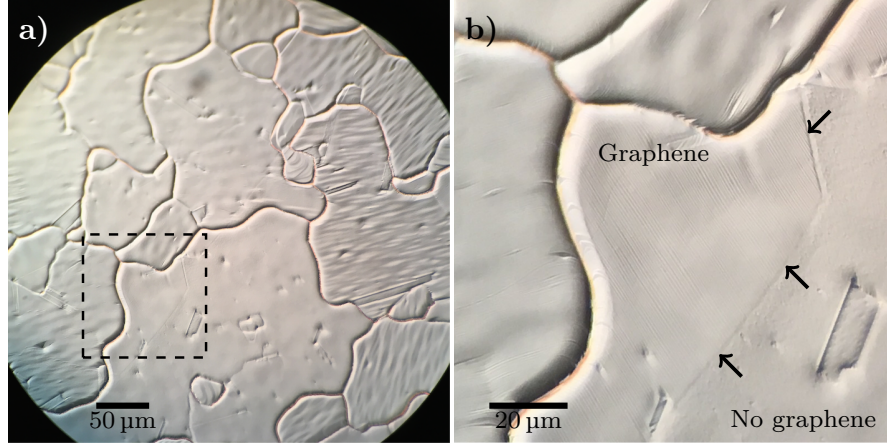


Figure 3.15: *Direct visualization of graphene as-grown on a Cu film. a) Optical microscope image of the Cu surface. b) Higher magnification image of the Cu surface area referenced by the dashed square in (a). Black arrows serve as visual guides to locate graphene.*

Intentional selective Cu surface oxidation

To enhance the contrast between the Cu surface areas that are covered by graphene and those that are not, one can proceed to the intentional selective oxidation of copper. As graphene is impermeable to gases, it protects the underlying Cu surface from the exposure to oxygen present in the atmosphere. Heating the synthesis substrate in the presence of oxygen, typically on a hot plate in ambient air at $T \geq 150$ °C for a few minutes, leads to a slight oxidation of the Cu surface which is not covered by graphene.

This direct visualization technique has been first employed by Jia *et al.* [79] who also showed that the Cu selective oxidation could be done using an H_2O_2 solution. Depending on the grown Cu oxide layer thickness, the areas that are not covered by graphene appear reddish or greenish which significantly increase the contrast as shown in Fig. 3.16a and 3.16b.

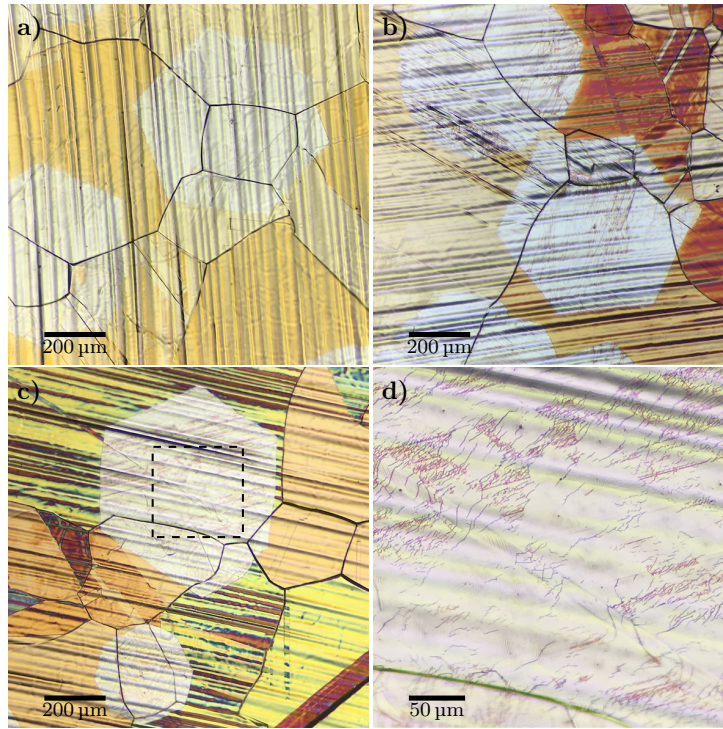


Figure 3.16: *Intentional surface oxidation-assisted visualization of graphene as-grown on a Cu foil. a-c) Optical microscope image of the Cu surface after an oxidation step of (a) 25 s at 220 °C, (b) 60 s at 220 °C and (c) 150 s at 250 °C. d) Higher magnification image of the Cu surface area referenced by the dashed square in (c) which shows multilayer regions with lateral dimensions of about 50 μm.*

Although this visualization method is rather limited, it can also be used to observe macro- and microscopic defects in the graphene film and reveal the presence of multi-layer areas. This can be achieved by heating the catalytic substrate at a higher temperature (typically $T \geq 220$ °C). The oxygen is able to diffuse at the interface between the Cu surface and graphene's first layer, predominantly along the cracks and wrinkles

and unveil the few-layer areas as shown in Fig. 3.16c and 3.16d. These few-layer regions provide a better protection against oxidation than the first layer and maintain the underlying Cu surface reduced for prolonged Cu oxidation durations.

It is however worth mentioning that heating graphene in the presence of oxygen is not desirable as graphene can collect oxygen or water vapor by physisorption or chemisorption on its surface which leads to a drastic reduction of its physical properties.

Natural selective Cu surface oxidation

When the Cu/graphene samples are kept in ambient atmosphere at room temperature for a few weeks or months, graphene domains become visible through a natural selective Cu surface oxidation. Unlike intentional oxidation, natural oxidation makes the Cu surface underneath graphene appear reddish as shown in Fig. 3.17.

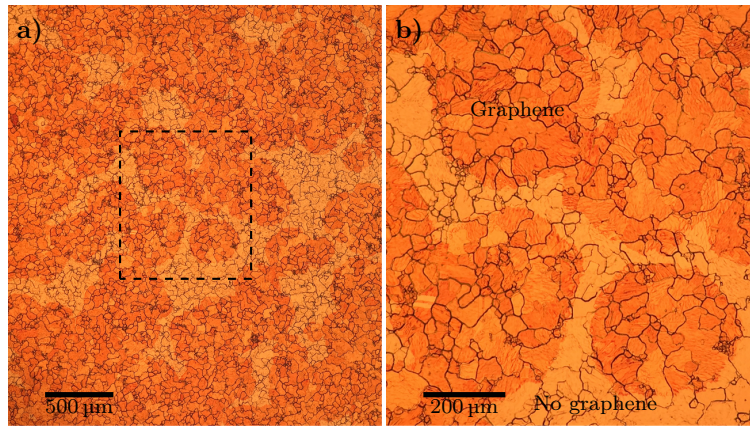


Figure 3.17: *Natural surface oxidation-assisted visualization of graphene as-grown on a Cu film after storing the sample in ambient atmosphere at room temperature for 8 months. b) Higher magnification optical image of the Cu surface area referenced by the dashed square in (a).*

Nowadays, the enhanced oxidation of graphene-coated Cu is still not clear and different mechanisms have been proposed. In 2013, two reports suggested that graphene acts as a conducting layer that promotes the electrochemical oxidation of the underlying copper and overcomes the self-passivation taking place in bare copper at room temperature [147, 148]. More recently, it has been suggested that the impermeability of graphene impedes the release of oxygen present in the Cu substrate [149]. Due to graphene, the out-of-equilibrium oxygen which diffuses through the Cu substrate thickness remains encapsulated at the Cu surface and accelerates the oxidation process.

Dark field imaging

Graphene can also be directly and rapidly observed on the Cu synthesis substrate using optical dark field (DF) microscopy. The clear contrast obtained between bare Cu surface and those covered with graphene is due to the difference in Cu surface morphology. The presence of graphene in close contact with the Cu surface helps maintaining the faceted structure of the Cu surface which has been induced during the high temperature annealing process under a reducing atmosphere [150]. The rough faceted Cu surface areas scatter incident light and make Cu surface areas covered by graphene clearly visible [151, 152]. Optical DF microscopy can also be used to identify the presence of additional graphene layers as their presence causes variations in the Cu step height [152]. Figure 3.18 shows that the optical contrast also depends on the underlying Cu surface crystallographic orientation.

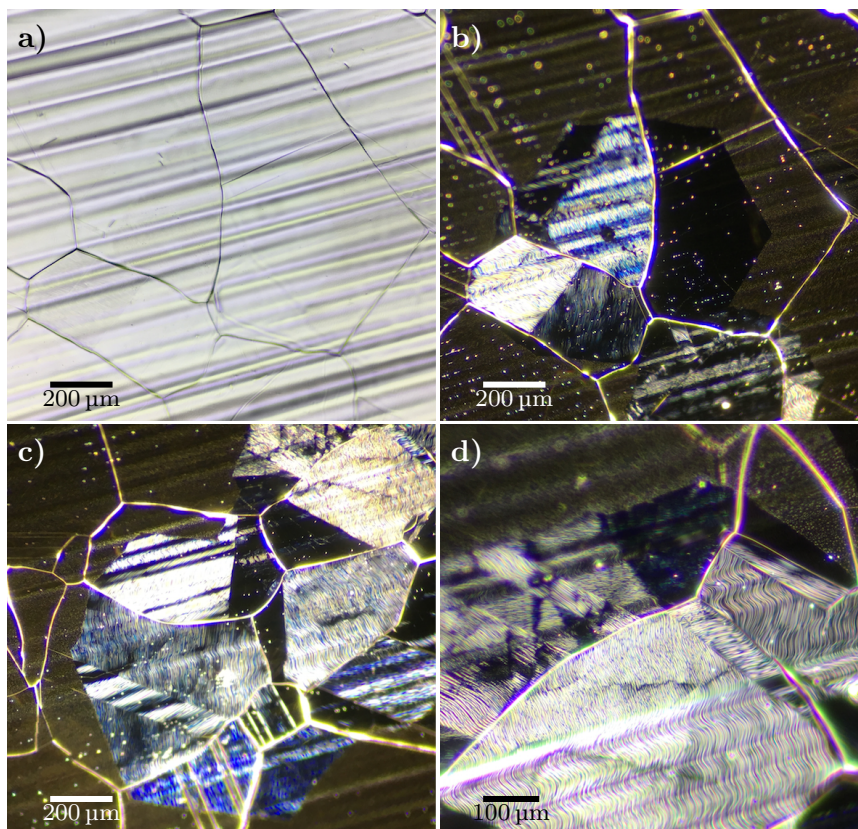


Figure 3.18: *Direct visualization of graphene as-grown on Cu foil. (a) Bright field and (b) dark field optical images taken in the same Cu surface area as indicated by the pattern of the Cu grain grooves. c-d) Dark field optical images taken at different Cu surface areas.*

Transferred on SiO₂/Si

Optical microscopy is of great interest as it offers a cheap, rapid and not destructive method to observe graphene characteristics over extended surface areas. Although direct visualization of graphene on the catalytic substrate is useful to observe individual graphene domain and thus determine their shape, size and density, it provides little information on the graphene thickness. Compared to directly observing graphene as-grown on the synthesis substrate, transferring graphene onto other substrates provides a better contrast imaging and can be employed most of the time to count the number of layers. The contrast, defined as the relative intensity of reflected light in the presence or absence of graphene depends on various factors such as the type of substrate, the thickness of the underlying transparent layer and the wavelength of the incident light. Blake *et al.* [153] used a Fresnel law-based model to calculate that SiO₂/Si substrates with oxide layers having a thickness around 100 and 300 nanometers are the most appropriate to observe graphene with white light. In contrast, a good optical contrast can be obtained with practically any SiO₂ layer thicknesses when using monochromatic light.

In the framework of this thesis, 90- and 300-nm-thick SiO₂/Si have been employed as substrates to characterize the thickness of the synthesized graphene film as shown in Fig. 3.19.

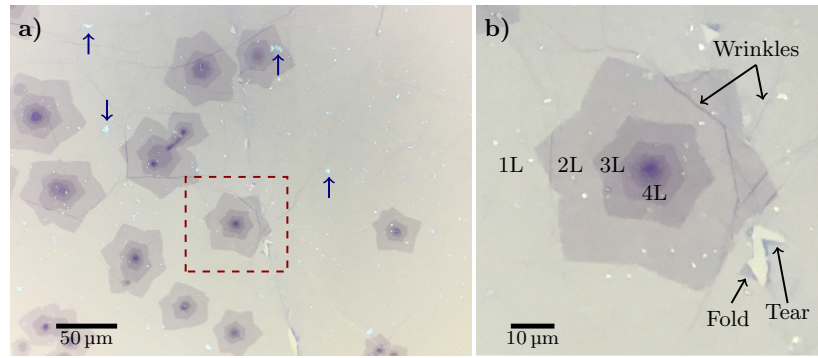


Figure 3.19: Visualization of graphene transferred onto a 300-nm-thick SiO_2/Si substrate. Owing to the enhanced optical contrast, various features such as cracks, tears, wrinkles and multi-layer regions can be observed with the optical microscope. Graphene transfer process is prone to leave some PMMA residues on the substrate surface as pointed out in (a) with vertical blue arrows. b) Higher magnification image of the surface area marked by a dashed red square in (a).

3.4.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a rapid, non-invasive and effective technique for imaging graphene on a wide variety of substrates. The SEM (Zeiss Gemini Ultra-55) is a versatile tool for detecting impurities, cracks, folds, wrinkles, voids and spatial variations of the number of layers at the micro- and nano-scales. The challenge for properly imaging graphene features lies in the facts that (i) probing the cross-section of the one atom-thick material is beyond the SEM resolution limitations, (ii) the SEM images predominately show the morphologies of the substrate beneath rather than the graphene itself given that the atomically thin film material is transparent to high energy electron beams, and (iii) graphene does not generate a strong contrast in SEM images because it has a very smooth surface. As a consequence, it is essential to use the proper SEM settings in order to obtain a sufficiently good contrast capable of revealing surface details including surface roughness, edges and additional layers.

Detector type

The SEM working principle is based on the emission (using a very fine heated filament) and the acceleration (to a desired kinetic energy) of electrons when propagating down through the SEM vertical column. In the Gemini column, a two-lens system is employed to focus the electron beam down to the substrate of interest with the desired spot size. The energetic bombardment of the incident electron beam on the sample generates several types of electrons which differ by their origin, energy and direction of radiation, and thus carry distinct information about the sample.

In this thesis, two different detectors have been employed to image graphene: a regular Everhart-Thorney (E-T) and an in-lens (also called in-column) detector. Both detectors collect the secondary electron (SE), that is, the electrons that are generated into the substrate bulk at different depths upon the radiation of the incident electron beam. The in-lens

detector efficiently collects the type I secondary electrons (SE1) that are generated close to the surface in the vicinity of the irradiated region and leave the surface with a high angle (i.e. almost perpendicularly to the surface). In contrast, the E-T detector collects the type II secondary electrons (SE2) that are generated from a deeper and wider volume inside the substrate than the SE1 and leave the substrate surface at a lower angle. As a consequence, the in-lens detector receives a signal enriched in SE1 which carries a high resolution surface-sensitive information of the sample while the E-T detector intrinsically provides lower-resolution topographical information. Therefore, the graphene film is mainly observed using the in-lens detector while the underlying substrate (Cu film/foil or SiO₂/Si substrates) is observed using the E-T detector as shown in Fig. 3.20.

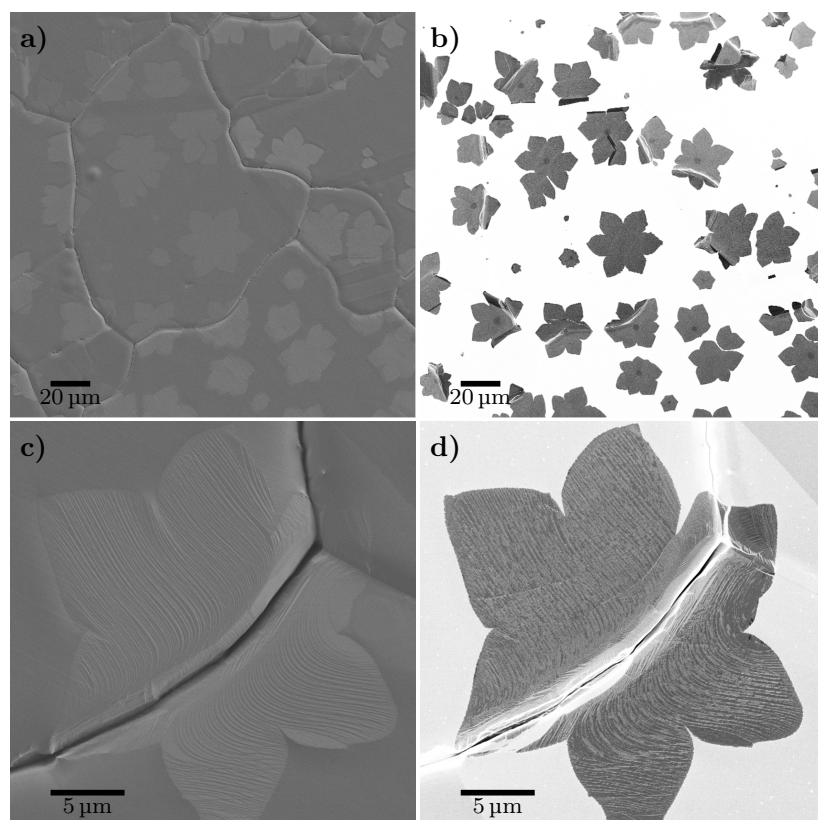


Figure 3.20: SEM observation of single-layer single-crystalline flower-shape graphene domains as-grown on a Cu film. (a,c) E-T and (b,d) in-lens SEM images have been taken in the exact Cu surface area. Higher magnification SEM images in (c, d) shows that the E-T detector can be used to observe very fine features of the Cu surface but does not provide any contrast for the presence of graphene compared to the in-lens detector. EHT=1 kV, WD=3 mm

Acceleration voltage and working distance

The acceleration voltage (Electronic High Tension, EHT) and the working distance (WD) are important parameters to properly image graphene. Operating the SEM equipment using a small working distance (between 1 and 5 mm) gives a better contrast for both detectors but more particularly for the in-lens detector that collects SE1 electrons which escape the sample perpendicularly to its surface.

SEM can be a very efficient tool to obtain quantitative information about the number of graphene layers on both Cu and SiO₂/Si substrates. The thickness contrast predominantly arise from the attenuation of secondary electrons emitted from the SiO₂/Si or Cu substrates by graphene layers present on the surface. Thicker stacks of graphene layers thus appear darker than a single-layer as shown in Fig. 3.21. When operating at low acceleration voltage, the low kinetic energy of incident electrons makes them interact with the sample near the surface rather than in its volume, thus giving a better spatial resolution. Moreover, as graphene mainly interacts with low-energy secondary electrons, the contrast is improved when using relatively small acceleration voltages.

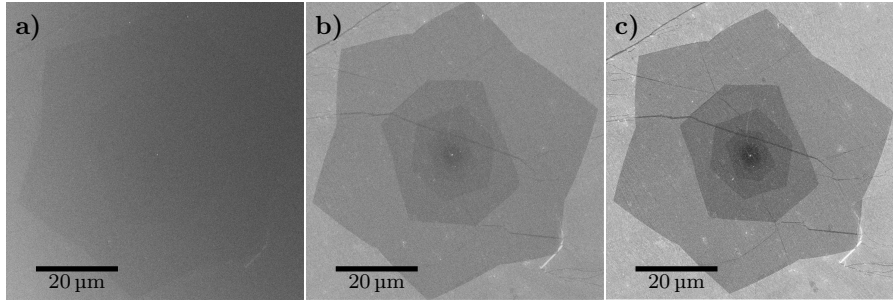


Figure 3.21: *In-lens SEM images of a stack of hexagonal shape single-crystalline graphene layers transferred onto a 300-nm-thick SiO₂/Si substrate. The images have been taken in the exact same location but using different acceleration voltages: 10, 5 and 2 kV for images (a), (b) and (c), respectively. WD=4 mm.*

The relatively rough Cu substrate under the as-grown graphene can alter the electronic signal detected by the SEM equipment and produce undesired artifacts on the SEM images in contrast to the flat and smooth surface of the SiO₂/Si substrate present under transferred graphene. However, directly observing graphene on Cu circumvents the use of the cumbersome transfer process and provides a conducting substrate that helps evacuating electrons from the surface. Indeed, the non-conductive nature of the SiO₂ layer causes an accumulation of electrons on the graphene that interacts with the incident electron beam and impairs the proper imaging of graphene. This phenomenon is a commonly known problem called the charging effect.

3.4.3 Raman Spectroscopy

Raman spectroscopy is a nondestructive versatile characterization tool employed to determine graphene number and stacking order of layers, structural quality and types of edge as well as the origin of perturbations including mechanical strain, doping and disorder. Raman spectroscopy measurements are based on the illumination of a sample with a monochromatic light (incident radiation) and the analysis of scattered radiation which results from various interaction events between photons, electrons and phonons within the material. Throughout this research, Raman measurements have been carried out using a LabRAM HR equipment (Horiba scientific) using a green laser (excitation energy of 2.41 eV or $\lambda=514$ nm, power level below 1 mW) on various graphene samples including as-grown on the Cu catalyst, transferred on arbitrary substrates or suspended.

Basic physics

Exposing a sample to an incident radiation leads to the re-emission of scattered radiation that exhibit either a different wavelength (Stokes and Anti-Stokes Raman scattering) or an identical wavelength (Rayleigh scattering). Rayleigh scattering (also called elastic scattering) takes place when an incident photon excites an electron-hole (e-h) pair from a ground state and the pair returns to its initial state by emitting a photon with identical energy but a different propagation direction. In contrast, Raman scattering is an inelastic scattering which implies that photons excite e-h pairs which, by transferring parts of their energy to phonons, return to a different state. Due to this energy transfer, the photon emitted upon the e-h recombination has a different energy. In the case of the Stokes process, which is the most likely to happen and thus the predominant phenomenon probed when performing Raman spectroscopy, the electron goes from a ground state to a higher energy vibrational state through the formation of a phonon and the emission of a photon having a lower energy than the incident one. In the case of the Anti-Stokes process, a phonon is absorbed by a e-h pair which then emits a photon of higher energy upon recombination.

The Raman spectra that are obtained with the Horiba equipment and the LabSpec software represent the plot of the intensity of scattered light as a function of the Raman shift which is the difference between the incident and scattered photon energy. The Raman shift units are usually expressed in cm^{-1} which can easily be converted in energy units using the relation³: $1 \text{ meV} = 8.0655447 \text{ cm}^{-1}$.

Exfoliated graphene

Before the first demonstration of the CVD synthesis of graphene, single and few-layer graphene flakes were obtained using mechanical exfoliation from natural graphitic mineral or highly oriented pyrolytic graphite (HOPG) which is a synthetic AB stacked graphite produced from carbon precursors heated up at very high temperature. The most prominent features present in the Raman spectrum of single-layer graphene are the so-called D-band, G-band and 2D-band appearing respectively at ~ 1350 , ~ 1580 and $\sim 2700 \text{ cm}^{-1}$ when using a laser energy of 2.41 eV. Two additional Raman features are sometimes observed at $\sim 1620 \text{ cm}^{-1}$ (called D'-band) and $\sim 2450 \text{ cm}^{-1}$ (called G*-band). Comprehensive explanations of the origin of these bands are beyond the scope of this thesis and can be found in recent studies [154, 155]. The examination of the intensity, width and position of these bands allows the thorough characterization of 2D graphitic specimens.

Figure 3.22 gives typical Raman spectra of single-layer graphene, bilayer graphene and graphite deposited on a 90-nm-thick SiO_2/Si substrate. Single-layer graphene has a sharp 2D-band which can be fitted with a single Lorentzian function and exhibits a full width at half maximum (FWHM) of $\sim 24 \text{ cm}^{-1}$. For single-layer graphene, the intensity of the 2D-band is greater than the G-band intensity. However, it has been demonstrated that the I_{2D}/I_G intensity ratio strongly depends on the underlying substrate [156, 157]. When multilayer graphene is obtained from exfoliation of crystalline graphite, it generally exhibits an AB (or Bernal) stacking which means that every individual graphene layers are

³ $E = h\nu = hc/\lambda$ with h and c corresponding to Planck's constant ($4.136 \times 10^{-15} \text{ eV.s}$) and the speed of light ($\sim 300000000 \text{ m/s}$), respectively.

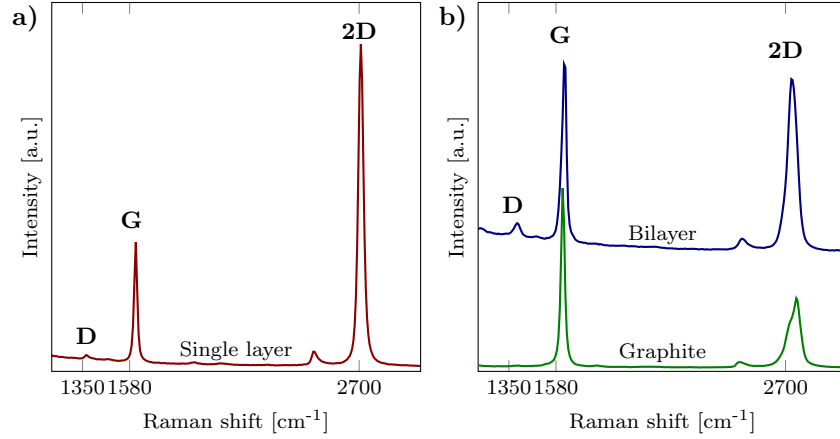


Figure 3.22: Raman spectra acquired on graphene deposited on a SiO_2/Si substrate by mechanical exfoliation of graphite. a) Single-layer graphene. b) Bilayer graphene (blue spectrum on top) and graphite (green spectrum at the bottom).

arranged in the direction perpendicular to the layer plane so that the vacant centers of the hexagonal rings of one layer are aligned with carbon atoms of the two adjacent graphene layers. For bilayer graphene with a Bernal stacking order, the 2D band has four components because of the electronic coupling between the two planes. As a consequence, the 2D band exhibit an intensity similar to the G-band, a full width at half maximum in the 40-60 cm^{-1} range and it can be fitted with four Lorentzian functions that are shifted in respect to the average frequency of the two main peaks by -44, -10, +10 and +25 cm^{-1} , respectively [158, 159].

Turbostratic graphene

In contrast to mechanical exfoliation of HOPG which results in multi-layer graphene predominantly exhibiting a bernal stacking, chemical vapor deposition on transition metals produces graphene layers having a random rotational orientation with respect to one another. This multi-layer graphene with no particular stacking order is called turbostratic graphene. Because of the absence of electronic interaction between graphene layers, the Raman spectrum of turbostratic multi-layer graphene looks more like the one of single-layer graphene rather than the one of AB stacked multi-layer graphene as the 2D band can be fitted with one single Lorentzian function. As an example, Raman spectroscopy maps have been acquired on the graphene sheet transferred on a 300-nm-thick SiO₂/Si substrate shown in Fig. 3.23b.

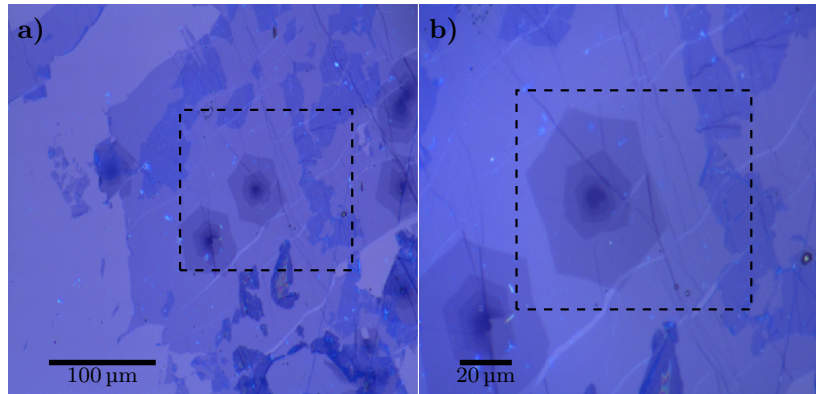


Figure 3.23: *Optical microscope images of a graphene sheet transferred on a SiO₂/Si substrate. b) Higher magnification image of the area marked by the dashed square in (a). The dashed square in (b) corresponds to the 70×90 μm² surface area that has been employed for the Raman maps shown in Fig. 3.24, 3.25 and 3.26.*

The sample shown in Fig. 3.23 has been selected as it contains single and multilayer graphene regions, wrinkles and cracks. Turbostratic multilayer graphene regions have been either naturally obtained by growing

one or two additional layer underneath the first graphene layer during the CVD process or artificially produced by tinkering with the graphene transfer step so that parts of the graphene sheet are torned up, washed away and re-deposited a bit farther on top of other graphene layers.

Figure 3.24 shows the maps of the D, G and 2D band peak intensities extracted from 6300 individual Raman spectra acquired in the $70 \times 90 \mu\text{m}^2$ surface area shown in Fig. 3.23b. The inter-spacing between individual punctual measurements is chosen to be one micrometer as it corresponds to the spot size of the laser on the sample surface. Although some features such as cracks, wrinkles and the different layers can be distinguished, these maps are not directly helpful to rigorously characterize the graphene sheet.

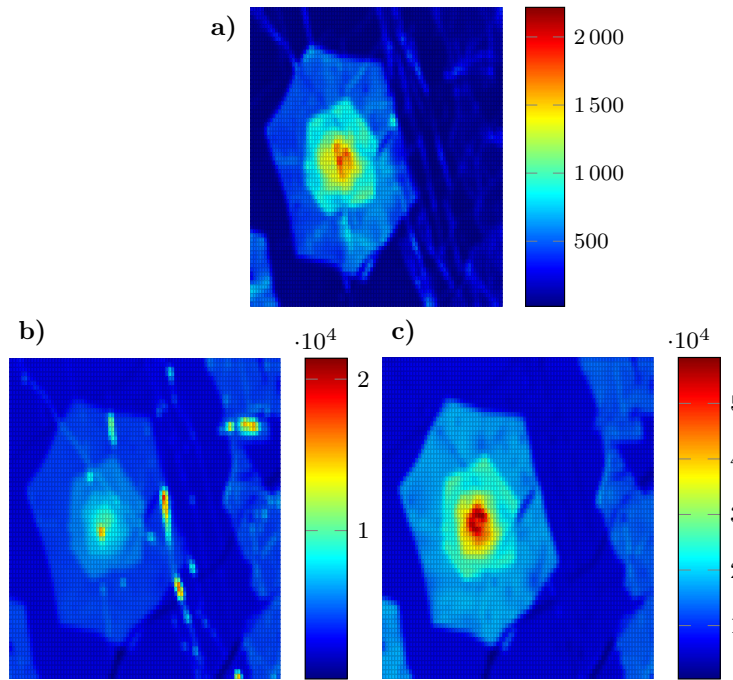


Figure 3.24: Raman maps of the (a) D band, (b) G band and (c) 2D band peak intensities acquired in the surface area marked by the dashed square area in Fig. 3.23b.

As these 3 maps have been extracted from the same series of Raman spectra, that is, the D, G and 2D bands have been acquired simultaneously, it is more meaningful to consider mapping the D-to-G (I_D/I_G) and 2D-to-G (I_{2D}/I_G) peak intensity ratios as shown in Fig. 3.25. Figure 3.25a exhibits a very low D-to-G peak intensity ratio which indicates that the disorder-induced D peak is very weak. Such small I_D/I_G ratios prove that the graphene sample is almost defect-free besides the presence of cracks and wrinkles that have been introduced during the transfer process and that are visible on the optical images [154]. By comparing Figs 3.24a-b with 3.25a, it can be observed that the increasing I_D/I_G ratio with the number of layers is mainly caused by an increase of the D peak intensity. Interestingly, the artificial additional layer that has been washed away and redeposited seems to have the opposite behavior as the wrinkles under the artificial layer feature a lower I_D/I_G ratio.

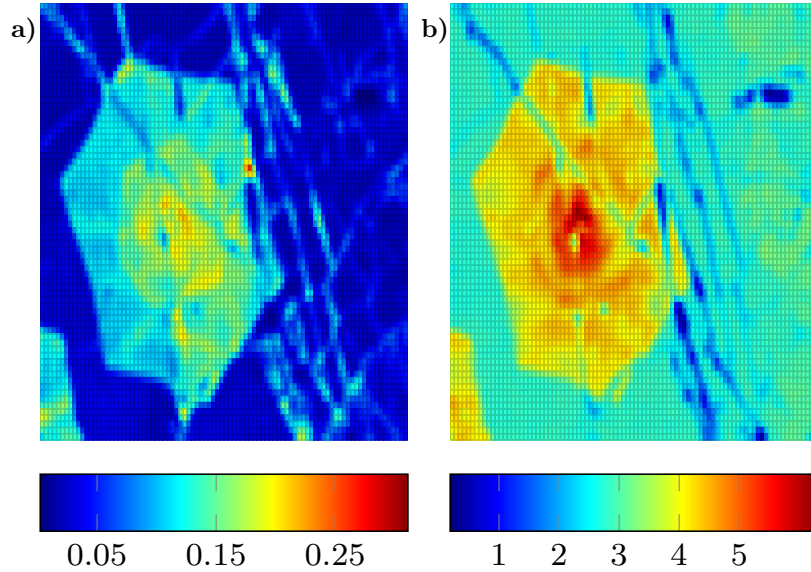


Figure 3.25: Raman maps of the (a) D-to-G, (b) 2D-to-G peak intensity ratios acquired in the surface area marked by the dashed square area in Fig. 3.23b.

The Raman map displayed in Fig. 3.25b shows that the single-layer graphene region exhibits a I_{2D}/I_G ratio superior to 2 which is in good agreement with the literature [158,159]. Figure 3.25b also shows that the I_{2D}/I_G ratio increases with the number of layers, regardless of whether it has been produced during the CVD or during the transfer process.

Initially, it was believed that turbostratic graphene had a FWHM_{2D} in the $\sim 45\text{--}60\text{ cm}^{-1}$ range and a 2D-to-G band intensity ratio much smaller than its AB stacked counterpart [154]. However, it has been later reported that the Raman signatures are sensitive to the electronic coupling between the graphene layers which strongly depends on the relative rotation angle between the top layer and the underlying additional layers [160–163].

The relative rotation angle has been demonstrated to affect the peak position, the 2D band FWHM, and the relative intensity of the G and 2D bands. Twisted bilayers graphene can be classified in 3 categories according to the relative rotation angle [160]:

$0^\circ \leq \theta \leq 5^\circ$: the strong inter-layer coupling within the bilayer results in Raman signatures exhibiting a I_{2D}/I_G ratio close to 1 and a FWHM_{2D} larger than the one obtained from single-layer graphene.

$7^\circ \leq \theta \leq 14^\circ$: the G band intensity is strongly enhanced due to resonance effects, making the I_{2D}/I_G ratio significantly inferior to 1.

$17^\circ \leq \theta \leq 30^\circ$: the graphene layers are decoupled or weakly coupled. The intensities of the G band and the 2D band are greater than single-layer graphene and the I_{2D}/I_G ratio is significantly greater than 1. Moreover, the FWHM of the 2D band is close or inferior to the one of single-layer graphene while its position is blue-shifted relatively to the one of single layer graphene.

For the bi-, tri- and few-layer graphene regions obtained upon the CVD process shown in Fig. 3.25b, the Raman signatures and more particularly the I_{2D}/I_G ratios indicate that the various layers are decoupled from each other. The twisting angle between the layers can also be determined optically by observing the domain orientations (see Fig. 3.23). As

hexagonal domain edges exhibit a zig zag structure, it can be observed that the second and fourth layers have the same in-plane orientation which is rotated by $\sim 30^\circ$ relatively to the third layer.

The graphene bilayer obtained during the transfer has a rather loose contact with the underlying graphene layer compared to as-grown turbostratic bilayer and the interface most likely contains residuals from the transfer process. As a consequence, the two layers do not interact together and are completely decoupled, thus resulting in Raman signatures almost identical to two nearby single-layer graphene sheets [161].

Figures 3.26a and 3.26b show that stacking decoupled graphene layers results in the narrowing of the 2D band and the blueshifting of its position, which is in good agreement with the literature [160, 162–164].

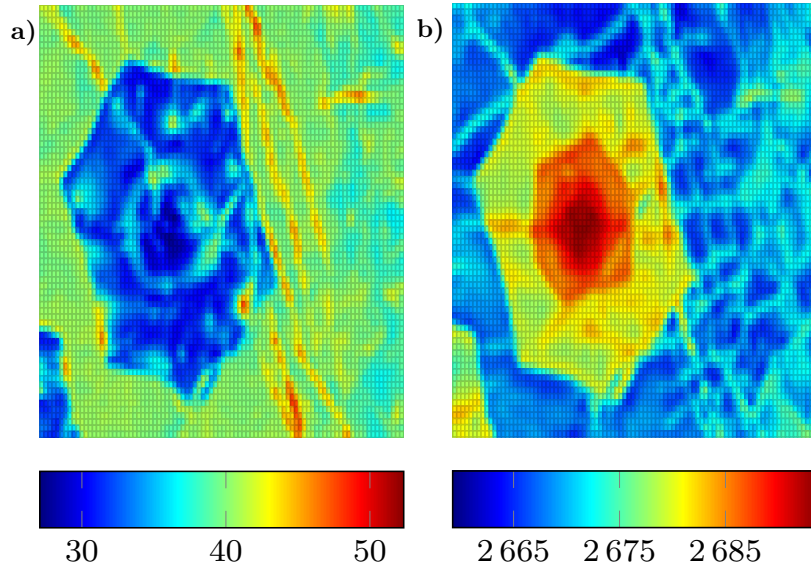


Figure 3.26: Raman maps of the 2D peak (a) full width at half maximum and (b) position acquired in the surface area marked by the dashed square area in Fig. 3.23b. The unit used for the scale of both images is cm^{-1} .

Analyzing the FWHM and the position of the main graphene Raman features can also give an insight about the doping level and the strain of graphene. As it has been explained in the preceding section, graphene transfer procedure is very likely to induce doping or mechanical strain in graphene. The FWHM of the G band is often in the $10\text{-}15\text{ cm}^{-1}$ range but it can change with strain, temperature and doping. Increasing the temperature generally leads to the redshifting of the G band position [165].

Applying an uniaxial tensile stress to graphene results in the redshifting of both G and 2D bands while a compressive strain causes the bands to blueshift [166,167]. When the strain exceeds 1%, the G band splits into 2 distinct sub-bands (G^+ and G^-) because of the symmetry breaking [166]. It has also been found that the position of the G and 2D bands can either increase or decrease depending on the doping intensity and whether the doping is p-type or n-type, respectively [167].

The blueshifting of the G and 2D bands can, for instance, occur upon the annealing ($T \geq 100\text{ }^\circ\text{C}$) of graphene transferred onto a SiO_2 substrate because of both, the more pronounced hole doping induced by the closer contact between graphene and the SiO_2 , and because of substrate-mediated mechanical compression strain in graphene [167].

When analyzing Raman signatures, it is also important to realize that the extracted graphene features are in general averaged over the laser spot size which is $1\text{ }\mu\text{m}$, typically. Variations of strain in graphene at the nanometer-scale, that is, at a sub-spot-size length scales, result in the broadening of the 2D band as well as the reduction of the 2D band peak intensity [168]. This phenomenon constitute the main reason explaining why the FWHM_{2D} and I_{2D}/I_G ratio is respectively larger and smaller for graphene deposited on SiO_2 compared with graphene deposited on h-BN [169].

CVD graphene as-grown on Cu

Raman spectroscopy can be carried out directly on the synthesis substrate after the CVD growth of graphene as shown in Fig. 3.27. Performing the Raman measurements directly on the Cu substrate has the advantage of circumventing the transfer process which is cumbersome, time-consuming and requires the dissolution of the synthesis substrate. Moreover, the transfer process is known to adversely impact the graphene physical integrity and cleanliness which thus cause the D-band to be more pronounced and the modification of the position and FWHM of the G and 2D bands.

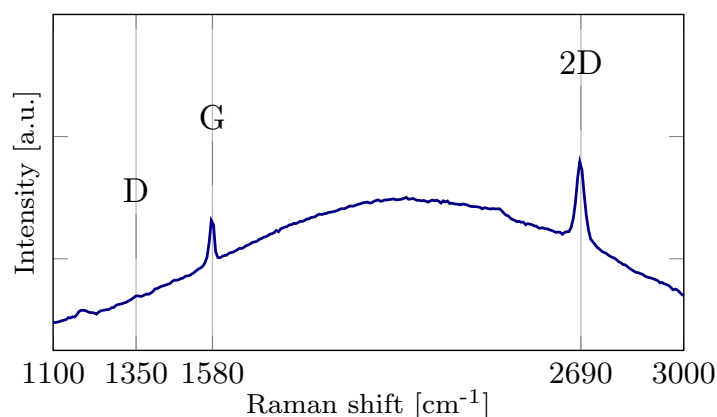


Figure 3.27: *Typical Raman spectrum acquired in the middle of a single-layer graphene domain as-grown on a thin Cu film.*

Counterbalancing with this advantage, the presence of the underlying Cu substrate adversely impacts the Raman measurements in different ways:

First, it generates a particular background in the spectrum which has to be removed in order to extract the intensities, the FWHM and position of the different graphene Raman features. Although it is rather fast and easy to remove the background from a single punctual measurement, the task gets exponentially more complex when dealing with large

collections of Raman measurements, which is the case when acquiring Raman mapping. The intensity of the background present in the Raman spectra can however be mitigated employing other laser energies [170]

The presence of the background in the Raman spectrum has also a detrimental effect on the signal-to-noise ratio as it makes the spectra intensity to saturate. Indeed, the signal-to-noise ratio usually depends on the laser power (tuned using filters), the grating, the acquisition time and the way the signal is averaged using multiple successive acquisitions in a single location. In order to have a smooth spectrum, these various parameters are adjusted in order to obtain graphene bands with a decent intensity. However, the software only allows a maximum intensity of about 69000 counts for the peak on top of the background, thus drastically reducing the intensity of the peaks that can be obtained.

Moreover, the polycrystalline nature of the synthesis substrate also impacts the Raman measurements as it has been demonstrated that the Cu crystalline orientation influences the I_{2D}/I_G intensity ratio [171]. It is also essential to perform the Raman analysis as soon as possible after the CVD process as Cu surface oxidation underneath graphene can take place in a few days, even at room temperature under ambient conditions [172]. This gradual surface oxidation (mainly Cu_2O) tends to reduce the electronic coupling between graphene and the underlying substrate and consequently causes the I_{2D}/I_G ratio to increase over time [173]. Furthermore, the strong coupling between graphene and the underlying Cu can result in both graphene doping through charge transfer and strain induced during the cooling down of the CVD process due to different thermal expansion coefficients [174, 175].

Finally, the rough Cu substrate surface morphology is not suitable for conducting large-area Raman maps as the distance between graphene and the lens strongly varies with the location.

3.4.4 Atomic Force Microscopy

Atomic force microscopy (AFM) is an efficient technique to get an estimation of the thickness of a graphene film and its surface topography at the nanometer scale. This technique is thus particularly interesting to identify graphene number of layers. The fundamentals of AFM rely on the movement of a sharp probe (tip attached at the free extremity of a cantilever) brought in close contact with the sample. When the probe and the sample move in relation to each other in a raster pattern, the equipment takes a series of data in discreet locations (pixels). These data are acquired through the cantilever displacement sensor that monitors the deflections of the cantilever free end when interacting with features on the sample surface.

In this thesis, the AFM images were collected using a Dimension Icon Instrument (Bruker) in air with the PeakForce Tapping (PFT) mode and ScanAsystTM (SA). Compared to the widely used contact mode which inherently exerts a lateral force on the sample and could damage graphene when dragging across the surface, PeakForce tapping mode intermittently contacts the sample and avoid lateral forces. In PFT mode, the piezoelectric transducer connected to the fixed end of the cantilever modulates the vertical position of the tip in a sine wave fashion with a frequency in the 1-10kHz range. Usually, when a tip approaches the sample surface, it experiences long-range van der Waals attraction forces that bring the tip into contact with the sample. Once in contact, the short range Coulomb forces dominate and repel the tip away from the surface. Owing to an algorithm that recognizes the local peak force, the system can map the surface morphology with high accuracy.

Figure 3.28 shows typical AFM images acquired on the surface of a graphene sample transferred on a SiO₂/Si substrate. Graphene wrinkles appear as white sharp lines while cracks appear as darker stripes with a width of several hundreds of nanometers.

In order to determine the thickness of the graphene film, it is preferable to scan across a graphene crack which constitutes a clean cut in the

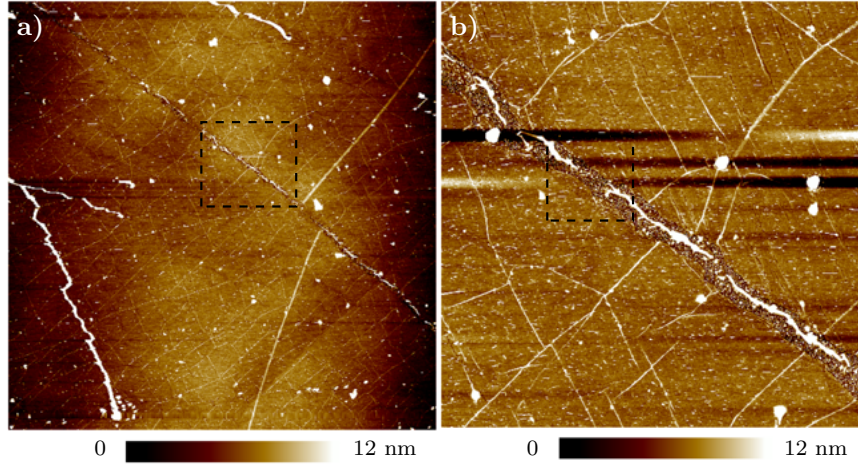


Figure 3.28: *PeakForce Tapping mode AFM images obtained onto a single-layer graphene sheet transferred on a SiO_2/Si substrate. a) $50 \times 50 \mu\text{m}^2$ surface area. b) $10 \times 10 \mu\text{m}^2$ surface area corresponding to the dashed square in (a).*

graphene rather than graphene domain edges that are more often jagged, torn up or simply not lying well in contact with the underlying substrate. The determination of an appropriate location to perform high accuracy AFM measurements often requires the successive acquisition of several maps with decreasing surface areas. Once the proper location is selected, a high accuracy AFM map can be acquired (see Fig. 3.29a) and a height profile can be extracted across the crack as shown in Fig. 3.29b.

The height difference between the top of graphene and the bottom of the crack is about 1.3 nm which is about 4 times the theoretical value of 0.34 nm referenced for the inter-plane spacing of graphite in the literature [176]. The obtained value however is in good agreement with other reports that also transferred graphene using the PMMA-assisted method [177, 178]. AFM measurements of graphene thickness can be influenced by the interactions between the graphene and the substrate and/or between graphene and the AFM tip, which can depend on the substrate surface energy or the graphene preparation method.

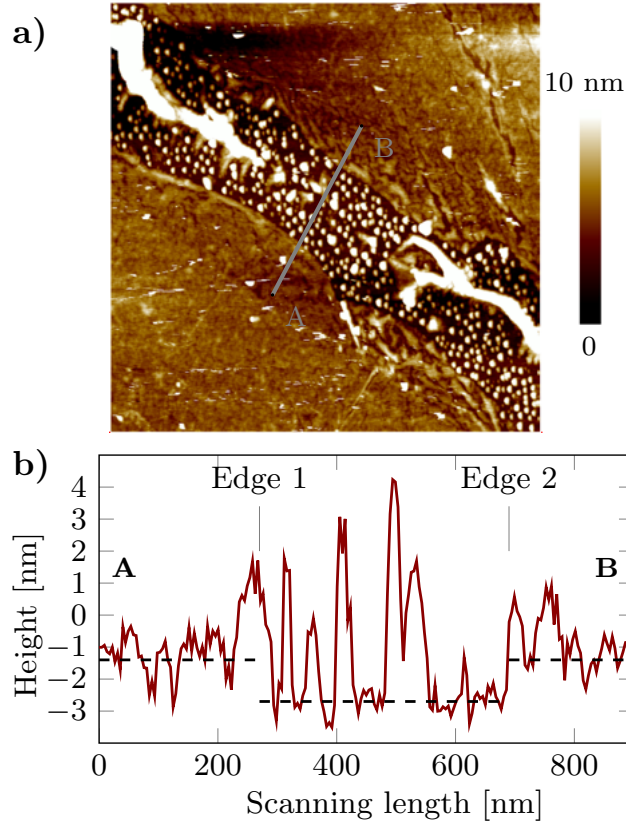


Figure 3.29: *Determination of graphene film thickness using AFM. a) $2 \times 2 \mu\text{m}^2$ PFT mode AFM image obtained in the dashed square area of Fig. 3.28b. b) Height profile performed across the crack (along the grey AB axis) shown in (a).*

The wet transfer method is very likely to create an inter-plane layer with adsorbates or trapped molecules that create a buffer between graphene and the substrate, hence causing the overestimation of the AFM measurements.

Chapter 4

Preliminary results and surface confinement

This chapter presents the preliminary experiments that have been conducted at the early stage of development of the CVD synthesis and describes the various challenges that have been addressed in order to produce graphene. In particular, this chapter exposes the first graphene results that motivated the customization of the CVD set-up (see chapter 5) and the use of fused quartz wafers instead of oxidized silicon wafers as substrates for growing graphene on Cu film. This chapter is divided into four sections. Section 4.1 briefly shows the first graphene growth experiments that have been conducted on Cu foils. Section 4.2 describes the various challenges that have been addressed in order to produce graphene on thin Cu films. Section 4.3 then reviews the various advantages stemming from using Cu surface confinement. Sections 4.3.2 and 4.3.3 put the obtained results in relation with the literature that, in some extent, also observed Cu surface confinement effects. Finally, Section 4.4 outlines the important findings and key process parameters that are essential for successfully depositing high quality graphene.

4.1 Preliminary growth results on Cu foils

As explained in the preceding chapter, the initial CVD system that was operated at the early stage of this thesis was quite simple. The CVD protocol was mainly based on previous CVD works reported in the literature before 2013 and consisted of four consecutive steps: the CVD furnace warming, the Cu annealing, the graphene growth, and the CVD furnace cooling as shown in Fig. 4.1. As the global pressure in the CVD furnace could only be adjusted by tuning the coarse throttle valve, graphene synthesis experiments were exclusively performed under LP-CVD conditions with a global pressure varying in the 0.5 - 2 mbar range depending on the total gas flow injected in the furnace. The CVD furnace was warmed up from room temperature to the growth temperature ($T_{\text{gr}}=1000\text{ }^{\circ}\text{C}$) within 80 min and maintained at high temperature for the Cu annealing and the graphene growth steps. As the CVD furnace does not possess a cooling system, the furnace cooling occurs by heat diffusion and loss through the ceramics surrounding the tube. This step takes about 80 min to cool down from $1000\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$. At $400\text{ }^{\circ}\text{C}$, the furnace lid can be opened to enhance the cooling rate, thus enabling the furnace to reach room temperature in about 40 min. The 40-min-long high-temperature plateau used for the Cu annealing step allows the Cu microstructure to evolve and reach a more stable configuration consisting of Cu grains extending over several tens or hundreds of micrometers. As explained in section 3.2, it is more beneficial for the graphene growth to take place on a rather stable catalyst rather than on a catalyst that is significantly evolving as the graphene growth proceeds.

Figure 4.2 depicts the CVD conditions that could be achieved with the initial CVD system as a function of CH_4 and Ar/H_2 gas flows. The turbo-molecular pump throughput is limited to a total gas flow of about 70 sccm which means that the Ar/H_2 gas flow can only be increased at the expense of the CH_4 gas flow and vice-versa. Moreover, the mass flow controllers can only ensure repeatable gas flow rates if they exceed 5% of their full-scale. The pure CH_4 and the diluted Ar/H_2 (5%) gas feedstocks could thus only cover a narrow H_2 -to- CH_4 ratio in the 0.008-0.65 range.

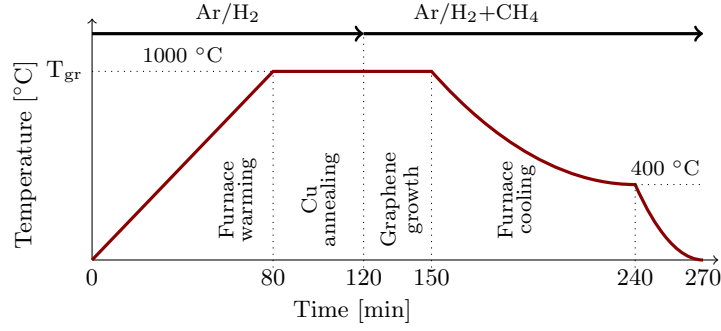


Figure 4.1: Temperature and gas flow profiles used for the first graphene growth CVD experiments on Cu foils.

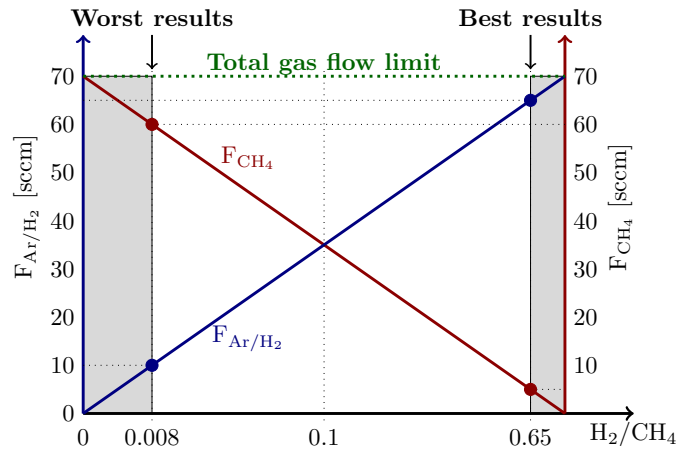


Figure 4.2: Schematic representation of the growth conditions that could be adjusted using the initial CVD setup. Best and worst growth results are obtained using H_2 -to- CH_4 ratios of 0.65 and 0.008, respectively.

Although the CVD system was quite limited, the graphene growth was taking place of both surfaces of the Cu foil that was placed in a ceramic boat when loaded in the CVD furnace. Intriguingly, the Cu foil backside was covered with graphene exhibiting domains having a pretty well defined shape compared to graphene that was growing on the Cu foil topside as shown in Fig. 4.3. The graphene growth outcome present on the Cu foil topside surface is rather difficult to interpret given the small size of continuous graphene islands (dark regions) and the significant amount of defective graphene exhibiting a high density of edges (appearing as white lines). Prolonging the growth duration resulted in a continuous graphene layer on both surfaces. Despite appearing highly similar when observed using the SEM, the analysis of the continuous graphene layer with Raman spectroscopy was showing a more frequent and more pronounced D-band on the Cu foil topside compared to the backside. Given the narrow experimental range for the H_2 -to- CH_4 ratio, tuning the parameters from the worst case to the best case scenario had a rather limited impact as it was only improving the graphene domain size by about 2-3 microns on average.

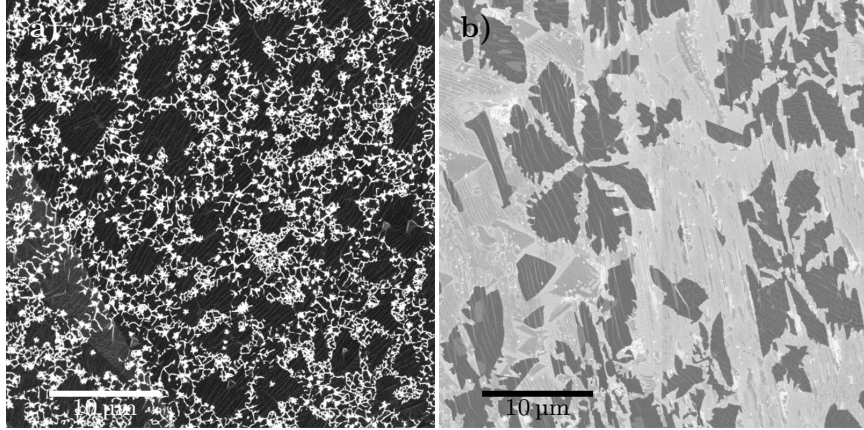


Figure 4.3: *In-lens SEM images of graphene grown on Cu foil ($t_{gr}=20$ min, $R=0.65$, $P_{gr}=2$ mbar: a) topside, b) backside.*

The lower graphene quality obtained on the Cu foil topside was thus attributed to unfavorable conditions in the vicinity of Cu surface during graphene growth. More particularly, it was believed that Cu foil top surface was experiencing a high Cu sublimation rate that was making the Cu foil surface less stable and competing with the graphene formation. The high Cu sublimation is caused by both high temperature conditions that favor a relatively high Cu vapor pressure (see Fig. 4.4) in the vicinity of the Cu surface and the low pressure conditions lead to an increased mean free path of gas molecules and help the Cu vapor escaping the vicinity of the Cu surface. Moreover, the Cu foil top surface is subjected to the gas flow mainstream that carries away the Cu vapor and forces the Cu foil to further sublime in order to establish the thermodynamic equilibrium between the Cu solid and gas phases.

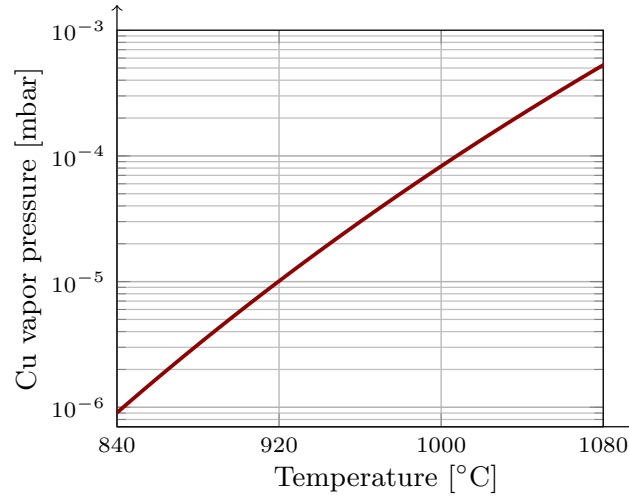


Figure 4.4: Plot of Cu vapor in equilibrium with Cu solid phase as a function of temperature calculated from ref. [179]. The Cu vapor exponentially increases with the temperature and varies by 3 orders of magnitude in the temperature range allowing graphene deposition using methane on Cu substrate.

When the graphene growth step was performed under lower global pressure ($P_{gr}=0.5$ mbar), it was observed that graphene could only grow on the Cu foil backside as shown in Fig. 4.5. This observation suggests that increasing the Cu sublimation rate can even result in the suppression of graphene growth. At that point, it was thus believed that there exists a competition between the Cu foil sublimation and the formation of graphene on the Cu surface. The next section presents additional experiments and observations that provide a better understanding of the various mechanisms playing a role in the growth of graphene.

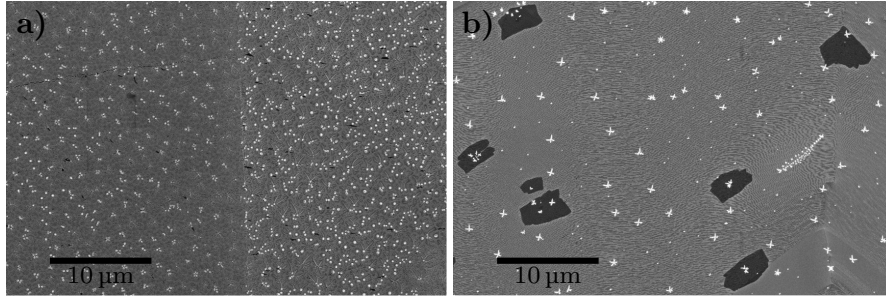


Figure 4.5: *In-lens SEM images of graphene grown on Cu foil (a) topside and (b) backside with $t_{gr}=20$ min, $R=0.65$ and $P_{gr}=0.5$ mbar.*

4.2 Preliminary growth results on Cu films

Growing graphene on Cu films pre-deposited on a thermally oxidized silicon wafer rapidly appeared to be more complicated than growing it on Cu foils. This section covers the most fruitful experiments that contributed to produce better quality graphene and helped better understanding graphene growth mechanisms.

4.2.1 CVD protocol and Cu film thickness

The first step to produce graphene on thin Cu films consists of determining experimental conditions that maintain the Cu film physical integrity throughout the CVD protocol. After a few CVD experiments, it rapidly appeared that the low pressure and high temperature conditions required to grow graphene were having harmful effects on the Cu film stability. Cu films with thicknesses ranging from 100 to 500 nm were dramatically damaged and no graphene could be synthesized. The CVD protocol has thus been adjusted to reduce the exposure to high temperatures and avoid the evaporation loss that leads to Cu film thinning, voiding, fingering and solid-state dewetting as shown in Fig. 4.6.

The more adapted CVD protocol, displayed in Fig. 4.7, is characterized by a steeper warming ramp and a Cu annealing step performed at a lower temperature¹. Compared with Cu foils, annealed Cu films contain Cu grains with rather limited lateral dimensions. Although the driving forces and kinetic processes are the same, the Cu grain growth in Cu films saturates more rapidly than in Cu foils. As a consequence, they do not need a long duration exposure to high temperature to reach a rather stable microstructure. This observation results from the fact that grain growth comes from the migration of Cu atoms from grains that have a less favorable crystallographic orientation (and thus a relatively high energy per atom on average) to grains having a more favorable

¹The heating step that ramps up the furnace temperature from 20 °C to 1000 °C is performed within 50 min. This represents a heating rate of about 20 °C/min which is the maximum rate recommended by the CVD furnace manufacturer.

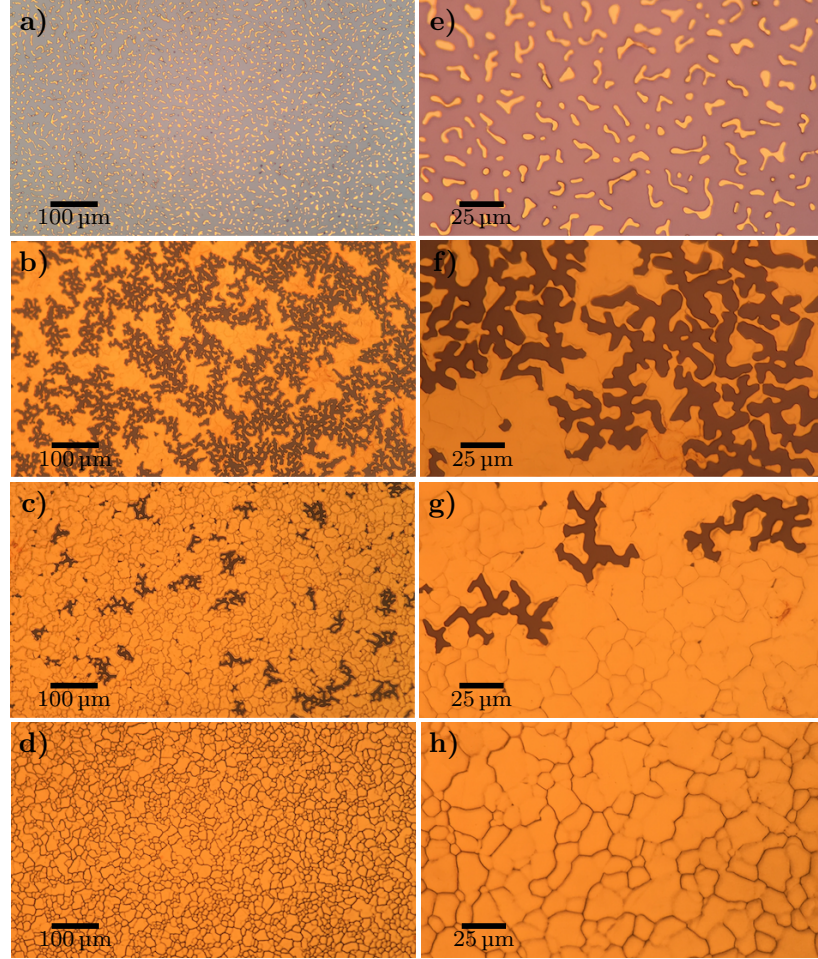


Figure 4.6: Optical microscope images of a 500-nm-thick Cu film pre-deposited on a Si/SiO₂ after thermal treatments similar to the CVD protocol presented in Fig. 4.1. The Cu films in a, b, c and d, have been warmed up within 80 min up to 1000 °C and then maintained at this temperature for 40, 15, 5 and 0 min, respectively before being cooled down to room temperature.

crystallographic orientation. This Cu atom migration occurs via Cu self-diffusion through the Cu grain boundaries. The cross section where this self-diffusion takes place is smaller for Cu films (which usually have a thickness inferior to one micrometer) than for commercial Cu foils that feature a thickness in the 7-100 μm range. When the Cu grains grow, the grain boundary grooves deepen and the cross-section available for self-diffusion reduces, thus impeding further Cu microstructure evolution.

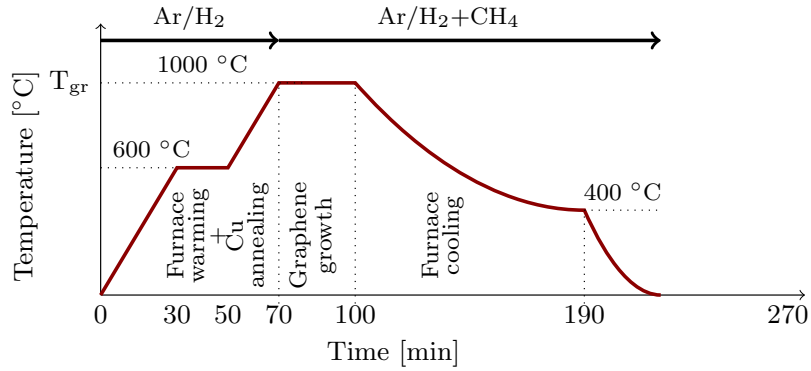


Figure 4.7: *Temperature and gas flow profiles used for the graphene growth CVD experiments while minimizing the Cu film exposure to high temperature.*

Performing the Cu annealing step at 600 °C instead of 1000 °C for 20 min seems to be sufficient for both, obtaining large and quasi-stable Cu grains and drastically reducing the Cu film voiding/dewetting upon the CVD process. Although the CVD warming and the Cu annealing steps have been adapted, the graphene growth step is the most delicate and detrimental stage for the physical integrity of the Cu film. Unfortunately, as explained in Chapter 2, the conditions favoring the formation of high-quality graphene are conflicting with those maintaining the Cu film physical integrity. More particularly, a higher growth temperature yields better graphene growth results in terms of domain density. Moreover, a long-duration graphene growth step is essential for growing large domains. As the graphene growth takes place and covers the Cu

surface, the Cu evaporation from the surface is gradually suppressed by the impermeable graphene film which makes the Cu catalyst more robust and capable of dealing with the exposure to high-temperature low-pressure conditions. However, the rapid coverage of the Cu surface and the production of large-area defect free domains require opposing CVD conditions. In order to make the catalyst more resilient to high temperature and low pressure thermal treatments, it has been decided to deposit a Cu thickness of at least 700 nm.

The Cu film evaporation loss can be drastically reduced using a high global pressure during the Cu annealing and graphene growth steps. However, the CVD equipment is not suited for performing the CVD protocol at a higher pressure. Another approach to address the Cu evaporation issues consists of using particular Cu catalyst configurations as described in the next sections.

4.2.2 Cu film confinement

Although the Cu film was making it through the CVD process without major damages, no graphene could be obtained on the thin Cu film, regardless the employed graphene growth conditions (with T_{gr} , P_{gr} and R ranging in the 980-1020 °C, 1-2 mbar and 0.008-0.65 ranges, respectively). Surprisingly, all of these conditions were producing graphene on both sides of the Cu foils.

As better graphene growth results were obtained on the Cu foil backside, it has been decided to flip the Cu film over and carry out CVD experiments with the Cu film facing the ceramic boat as illustrated in Fig. 4.8. Interestingly, this Cu film configuration was enabling the growth of graphene on the Cu film surface. However, that experiment was not highly reproducible as repeatedly reproducing the exact same experiment was leading to different graphene coverage. Graphene was only able to grow in the Cu film sample center and the Cu surface area covered by graphene was strongly dependent on how the Cu film was

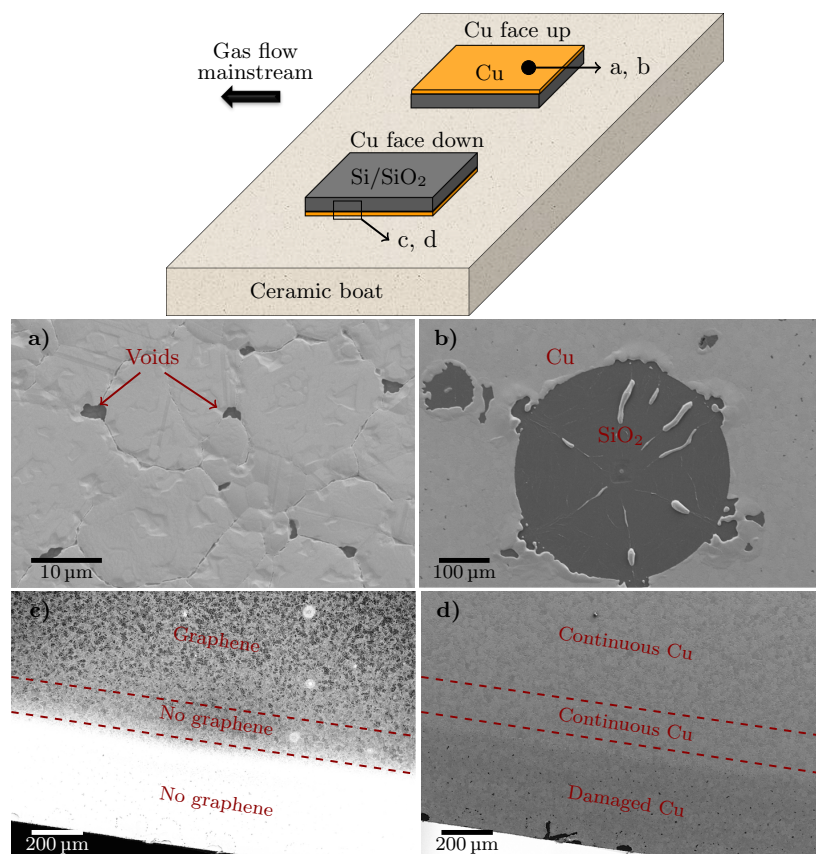


Figure 4.8: Schematic depiction of the Cu film substrates placed in the ceramic boat with the Cu film facing up or down. a-b) E-T SEM images taken on the Cu surface directly exposed to the CVD atmosphere illustrating the various damages that have been observed. c) In-lens and d) E-T SEM images of the Cu surface (near the sample edge) in contact with the ceramic boat bottom during the CVD process. Graphene did not grow on the Cu surface facing up or near the edges of the Cu film facing down.

placed in the ceramic boat.

After a few CVD runs, it has been found that the lack of repeatability originated from the uneven bottom surface of the ceramic boat. This uneven surface was elevating/suspending some parts of the Cu samples and making the Cu surface to be less protected by the underlying surface.

In order to make the CVD experiments more reproducible, the ceramic boat has been replaced by a smooth and flat fused quartz wafer. This home-made sample holder was able to support larger samples (compared with a $2 \times 3 \text{ cm}^2$ sample in the ceramic boat) and allowed the repeatable growth of graphene over the entire Cu surface area except still a few hundreds of micrometers from the sample edges. In order to better understand why covering the Cu surface is a key process step to enable the growth of graphene on thin Cu film, another Cu film configuration has been employed as depicted in Fig. 4.9.

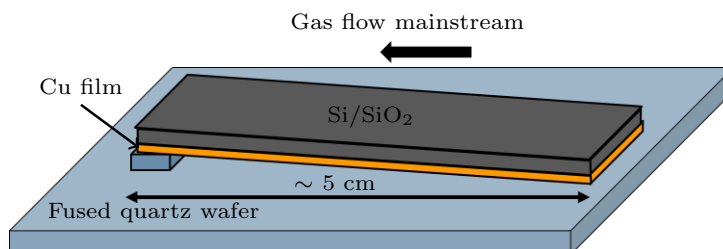


Figure 4.9: Schematic depiction the Cu film substrate configuration employed to create a gradient of Cu surface confinement along the catalytic sample.

This particular configuration has been devised in order to create a gradient of spacing between the Cu surface and the flat fused quartz support. Placing the Cu sample facedown in direct contact with the support on one extremity and elevating the other extremity with a $500 \mu\text{m}$ -thick piece of quartz forms a gradient of Cu surface confinement varying along

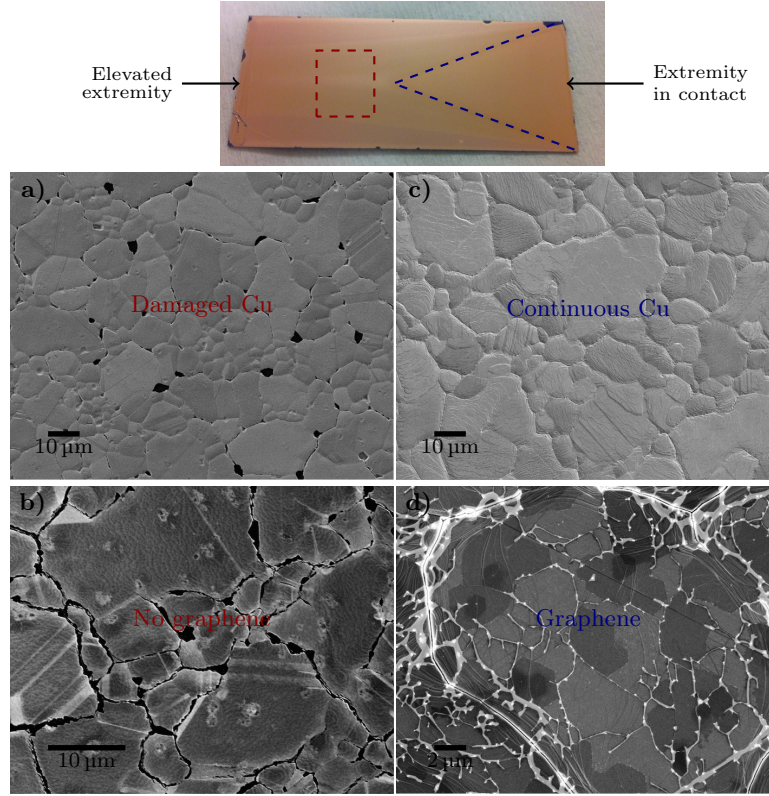


Figure 4.10: Photograph of the thin Cu film after the graphene growth using a gradient of confinement as shown in Fig. 4.9. (a) E-T and (b) in-lens SEM images taken somewhere in a non-confined Cu surface area (dashed red rectangle in the photograph). (c) E-T and (d) in-lens SEM images taken in a confined Cu surface area (dashed blue triangle in the photograph). a-b) Non-confined Cu surface is not covered by graphene and contains voids. c-d) Confined Cu surface is covered with graphene and does not exhibit any voiding or dewetting.

the sample length. It is worth noting that this configuration cannot be achieved using a Cu foil as the high temperature CVD process would make it soften and collapse to conform the underlying quartz surface. Figure 4.10 shows the resulting Cu sample after a classical CVD process as described earlier in this section (see Fig. 4.7). The Cu surface in the photograph exhibits different hues due to a spatial variation of the surface roughnesses or morphology. This surface morphology is visible in Figs. 4.10a and 4.10c. SEM images also show that graphene has only been able to grow in the Cu surface area that was in relatively close contact with the quartz surface (less than 200 μm) and away from the gas flow mainstream (see dashed dark blue triangle in Fig. 4.10).

These observations can also be explained by the competition between the Cu evaporation and the graphene growth on the Cu film. In its conventional configuration, the Cu film is in direct contact with the gas mainstream that carries away the Cu vapor and favors a relatively high Cu evaporation rate. In contrast, placing the Cu film in contact with another surface maintains the Cu vapor in the vicinity of the Cu surface which is thus more prone to establish a quasi-static equilibrium between the solid and gas phases of Cu. Consequently, the Cu vapor trapping or Cu surface confinement drastically suppresses the Cu evaporation and allows the graphene growth to take over. The Cu film hue spatial change corresponds to gas flow patterns along the surface and evidences Cu surface morphology spatial variations. The Cu film surface near the sample edges is rougher compared to the more confined areas as it experiences significant Cu evaporation enhanced by the gas flow mainstream.

Other Cu film configurations have also been investigated such as placing two Cu surfaces in direct contact with each other as shown in Fig. 4.11. This configuration gives the ultimate Cu surface confinement as both surfaces are smooth, flat and prone to release Cu vapor upon the high temperature CVD process. SEM pictures taken in various locations of the Cu surface clearly show that the graphene growth rate is enhanced in the center of the Cu sample compared with the rest of the sample. Yet again, this observation can be explained by the competition between the

Cu evaporation and graphene formation. Given that the Cu vapor can only escape by diffusing along the Cu/Cu interface prior to be released in the CVD furnace atmosphere at the Cu sample lateral sides, it is very likely that the partial pressure of Cu in the vicinity of the Cu surface is higher at the Cu sample center than at the Cu sample edges. The higher Cu partial pressure thus reduces the Cu evaporation rate and enhances the graphene formation.

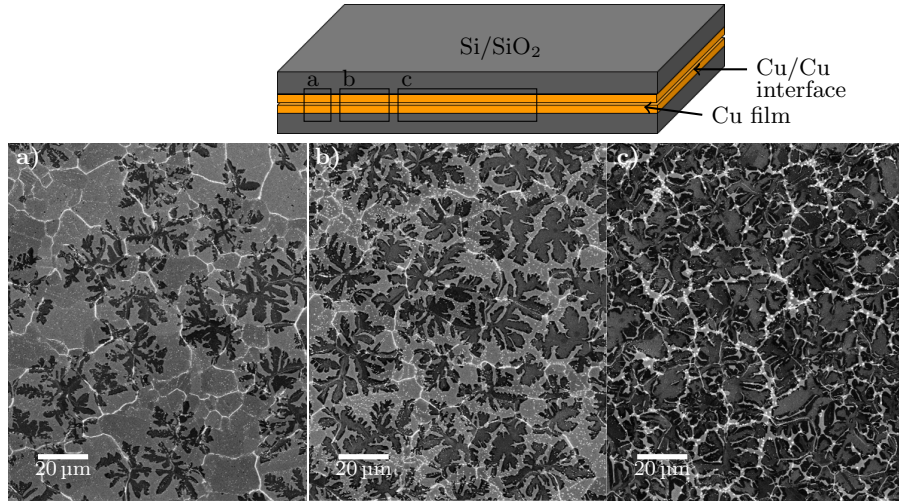


Figure 4.11: Schematic depiction of two Cu film substrates placed in close contact to obtain a high level of surface confinement. In-lens SEM images in (a), (b) and (c) have been taken on the Cu surface areas near the sample edge, at an intermediate location and at the sample center as illustrated by the frames in the depiction. The growth has been obtained using $t_{gr}=30$ min, $R=0.65$ and $P_{gr}=2$ mbar.

The spatial variation of graphene growth with the distance from the Cu edge is more pronounced when two Cu substrates are facing each other (Cu/Cu interface) compared with when one Cu sample is facing a catalytically inert quartz surface such as a quartz wafer.

4.2.3 Wafer-scale graphene growth

Now that the Cu samples are placed on a fused quartz wafer instead of inside a ceramic boat, samples with larger dimensions can be loaded in the CVD tube that has an inner diameter of 9.2 mm. When using an entire 3-inch-Cu/SiO₂/Si wafer (see Fig. 4.12), it appeared that the graphene can grow over most of the Cu surface area.

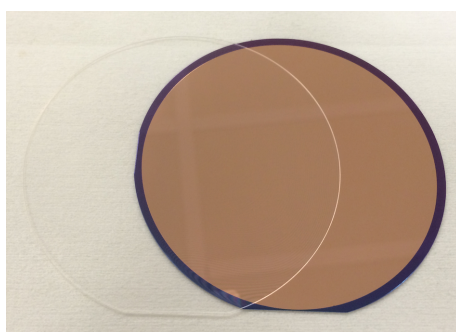


Figure 4.12: *Photograph of 3-inch fused quartz wafer deposited in direct contact with an entire catalytic substrate (800-nm-thick Cu film pre-deposited on a 300-nm-thick SiO₂/Si wafer). The two wafers are intentionally misaligned for the photograph in order to readily distinguish both wafers.*

As shown in Fig. 4.13, it appeared that the graphene growth rate (and thus the Cu surface area covered by graphene) increases with the distance from the Cu sample edges and reaches a maximum in the Cu sample center. This result indicates that a sufficient high amount of H₂ and CH₄ molecules have been able to diffuse over more than 3.5 cm along the interface between the Cu and the quartz surface despite the fact that the two wafers are separated by less than 5 microns. More interestingly, it can also be observed in Fig. 4.13 that the graphene growth front is less dendritic for domains growing near the Cu sample center than for those growing near the the Cu sample edges. This observation is rather surprising as larger domains tend to have more graphene front instabilities.

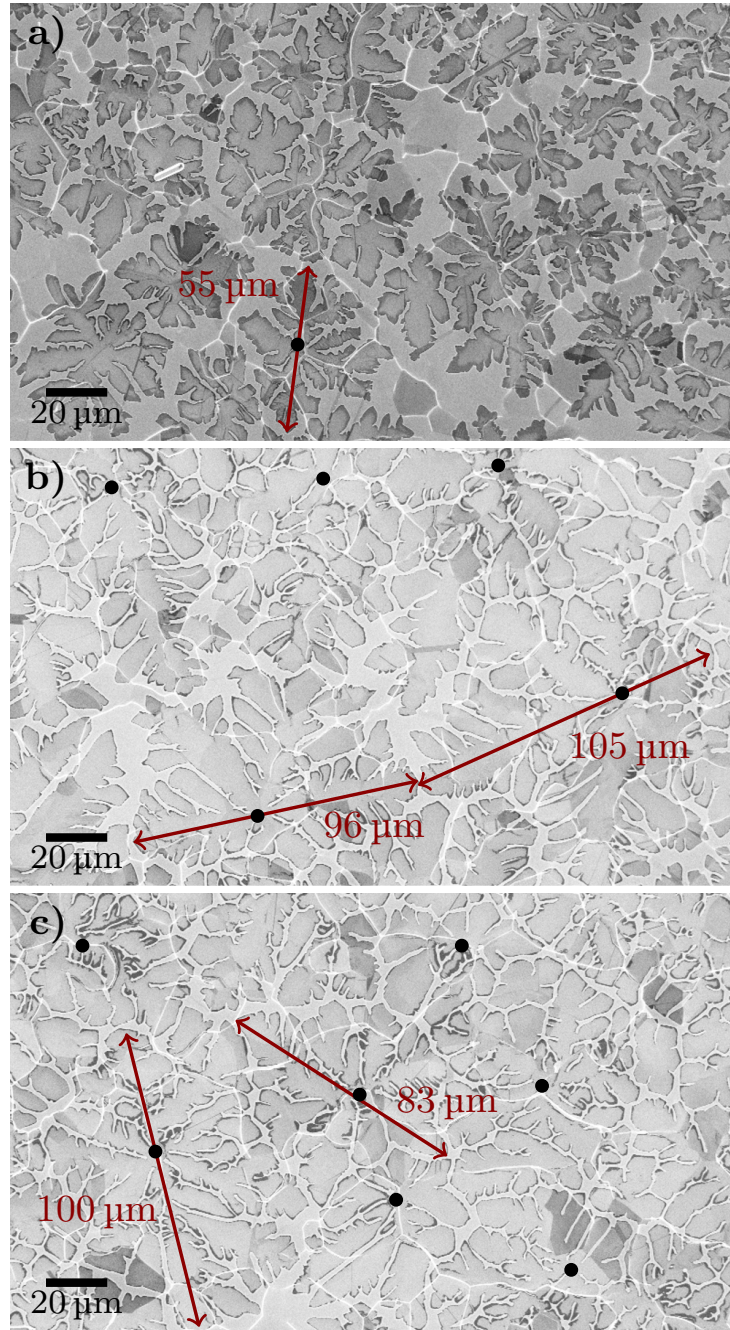


Figure 4.13: Graphene growth spatial evolution for a 3-inch Cu film wafer confined with a quartz wafer ($R=1.3$). SEM images taken on the Cu surface at a) 2.8, b) 2.0, and 0 cm from the wafer center, respectively. Black dots serve as visual guides for nucleation sites.

Finally, the lower nucleation site density obtained in the central region of the Cu wafer allows the domains to reach a lateral size exceeding 100 μm while those growing in the Cu sample periphery can only reach a dimension of about 50 μm before merging with adjacent domains.

The evolution of both the graphene growth front (and thus the graphene domain shape) and the nucleation site density with the distance from the Cu sample edge can be explained by a gradual modification of the gas phase composition in the vicinity of the Cu surface. Near the Cu sample edges, the gas composition in the vicinity of the Cu surface is rather similar to the one of the gas flow mainstream and contains a partial pressure of Ar, H_2 and CH_4 which is controlled by the mass flow controllers. In order to reach the center of the Cu sample, the various gas molecules have to diffuse along the interface. Due to their small molecular size, H_2 molecules have a higher diffusivity and can thus more easily travel along the interface compared to Ar and CH_4 molecules. On the other hand, the mean free path of gas molecules (which strongly depends on the global pressure) is inferior to 100 μm which suggests that the molecules will collide many times with the Cu and quartz surfaces before reaching the center of the catalytic substrate. As part of CH_4 molecules will be adsorbed by the Cu surface to contribute to the growth of graphene along the interface and as H_2 is a by-product of the graphene formation reaction, it is very likely that the H_2 -to- CH_4 ratio is greatly improved in the central region of the Cu sample compared to its periphery. The local improvement of the graphene nucleation site density and graphene growth front morphology can thus be explained by the local increase of the H_2 -to- CH_4 ratio and the local depletion of methane in the gas phase.

These new outcomes suggest to reconsider the aforementioned mechanism proposed to explain the enhanced graphene growth rate present in confined Cu areas. Although the Cu vapor trapping might play an important role in growing graphene, the increase of graphene growth rate observed in the center of confined Cu substrates can also be explained by the improved H_2 -to- CH_4 ratio. As explained in Chapter 2, hydrogen has a dual role in graphene growth as it serves as a co-catalyst for the graphene growth reaction and as an etching agent for graphene at the

edges of graphene domains. In general, increasing the hydrogen concentration boosts the graphene growth rate when the CVD process is achieved under low H_2 -to- CH_4 conditions while it slows down the growth when it is achieved under high H_2 -to- CH_4 conditions². Given the dendritic shape of graphene domains and the low H_2 -to- CH_4 ratio values that can be obtained with the initial CVD furnace setup compared to the literature (see tables in Chapter 2), it is evident that the H_2 -to- CH_4 ratio present in the gas mainstream of the CVD furnace is suboptimal. The enhanced growth rate present in the Cu sample center is thus consistent with an increase of the H_2 -to- CH_4 ratio.

4.2.4 Catalyst poisoning

Intriguingly, it appeared that surface confinement was not necessary anymore to grow graphene on Cu thin film when entire Cu/SiO₂/Si wafers were employed instead of cleaved pieces. However, the graphene growth results were not repeatable as similar CVD experiments applied on different individual catalytic wafers were producing different graphene growth results. In order to determine the mechanism responsible for the suppression of graphene growth when using cleaved Cu/SiO₂/Si samples instead of entire wafers, both samples have been loaded simultaneously into the CVD furnace so that they undergo identical CVD conditions and share the CVD atmosphere. When observing both samples by the means of the SEM, it appeared that no graphene was present on the surface of both samples.

After performing a few other similar experiments, it has been found that the major reason responsible for the absence of graphene on the Cu surface is the Cu catalyst poisoning by silicon. Cleaving the Cu/SiO₂/Si wafer into pieces opens up Si surfaces at the sample edges that are in direct contact with the furnace atmosphere during the CVD process. During the high temperature low pressure process, the Si surfaces are prone to release Si vapor into the CVD furnace. This Si vapor is carried

²Chapter 6 will show that the balance is not only dictated by H_2 -to- CH_4 ratio but also by the P_{CH_4} as well as the global pressure.

away by the flow mainstream and transported onto the Cu surface to form a Cu-Si alloy. This layer of Cu-Si alloy passivates the catalyst surface and prevents any graphene growth.

In theory, using an entire Cu/SiO₂/Si wafer protects the CVD atmosphere from a Si contamination but it represents a substantial risk in practice. Many elements can contribute to release Si inside the CVD atmosphere and jeopardize the CVD process:

1. **Direct release of Si in the CVD atmosphere:** Si vapor can be released into the CVD furnace atmosphere if the SiO₂ coating is removed. It has been found that just introducing a Si sample of about $1 \times 1 \times 0.38 \text{ mm}^3$ is enough to completely suppress the graphene growth over entire 3-inch catalytic substrates. It is thus essential to ban cleaved Cu/Si/SiO₂ samples from the CVD furnace. It is also essential to avoid any adventitious scratches in the SiO₂ layer during pre-CVD processes such as the standard cleaning or the Cu evaporation process. Cu surface poisoning coming from undesired Si vapor in the CVD atmosphere can be observed as it modifies the Cu surface roughness, makes the Cu film more prone to voiding and prevents the Cu grain growth (see Fig. 4.14).

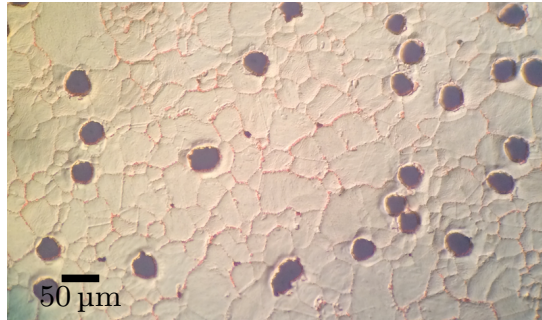


Figure 4.14: *Optical microscope image of a Cu film contaminated by Si vapor upon the CVD process.*

- 2. Cu-Si inter diffusion through the SiO₂ layer:** The high temperature required for the CVD process promotes the inter-diffusion of Cu in Si and vice-versa. If the SiO₂ layer is too thin or has a bad quality, the Cu film can diffuse through the SiO₂ layer and react with the underlying silicon substrate. It has been observed that if the Si substrate is in direct contact with the Cu film during the CVD process, it acts as a sponge which absorbs the Cu and swells. The increase of volume upon the absorption of Cu makes the SiO₂ layer crack, burst and produce a cascading effect that severely damages the substrate. For instance, Fig. 4.15 shows what happened when using a 90-nm-thick SiO₂ film instead of a 300 nm.

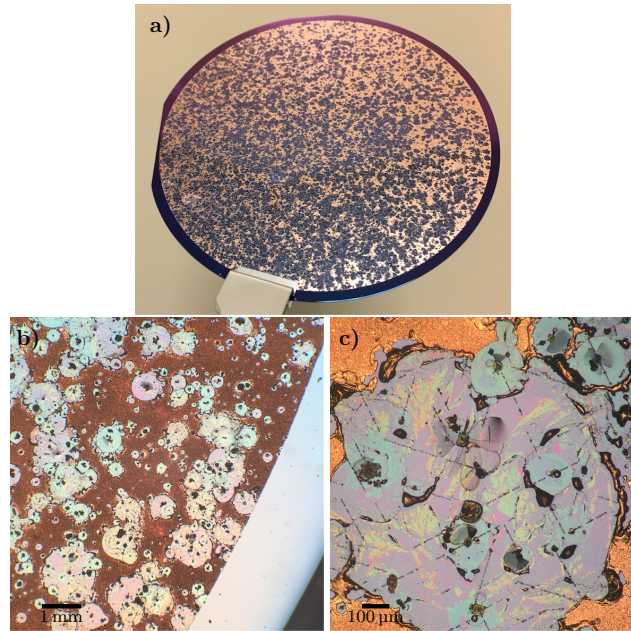


Figure 4.15: Photograph and optical microscope images of a Cu film substrate after attempting to grow graphene using a 90-nm-thick instead of a 300-nm-thick thermal oxide layer. Images (b) and (c) have been taken near the wafer edge. The absorption of Cu in the bulk of Si makes the SiO₂ film burst.

It is evident that the SiO_2 film cracking is due to inter-diffusion phenomena as the wafer periphery which has not been coated with the Cu film during the metallization process is crack-free.

3. SiO_2 layer bursting/cracking: The long-duration exposure to high temperature can make the SiO_2 layer burst by itself. This phenomenon is more prone to occur when employing a non-optimal thermal oxidation process for the Si wafer and at the Cu/Si/ SiO_2 backside due to its strong surface roughness. Figures 4.16a-b show the backside of a Si wafer that has been oxidized with a recipe alternating dry and wet oxidation process steps. Upon the CVD process, the high temperature causes the SiO_2 layer to burst in numerous places which thus become punctual sources of Si vapor.

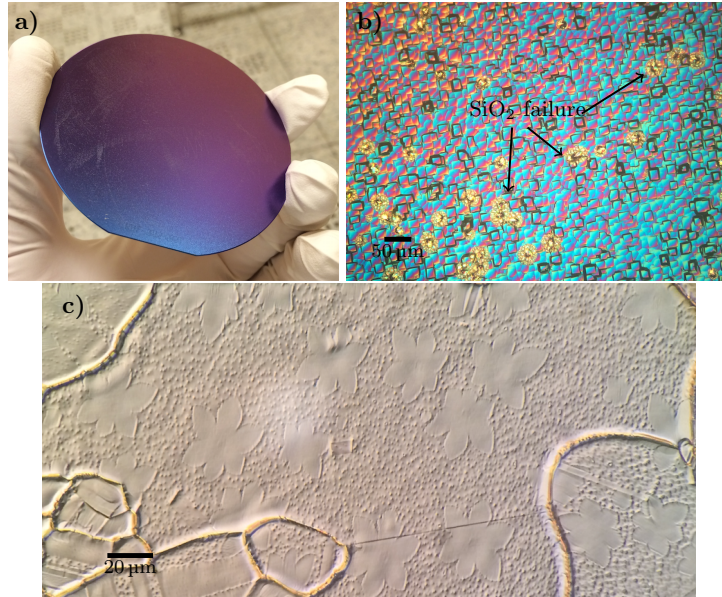


Figure 4.16: a) Photograph of the Cu/Si/ SiO_2 wafer backside after a CVD process. The whitish hue in (a) is caused by numerous burst shown in the optical microscope image in (b). c) Optical microscope image of the Cu surface when the Si contamination occurred at the end of the graphene growth step.

As this phenomenon takes place at high temperature, it mostly happens during the graphene growth process as shown in Fig.4.16c. As the Cu surface was Si-free at the early stage of graphene growth, the nucleation and growth of graphene were possible. Due to the impermeability of graphene, only the bare Cu surface gets contaminated by the Si vapor.

The high temperature can also either cause thermo-mechanical stress into the Cu/Si/SiO₂ system or make large samples buckle/bend under their own weight. These phenomenon contribute to the weakening of the SiO₂ layer and makes it more prone to cracking as shown in Fig. 4.17.

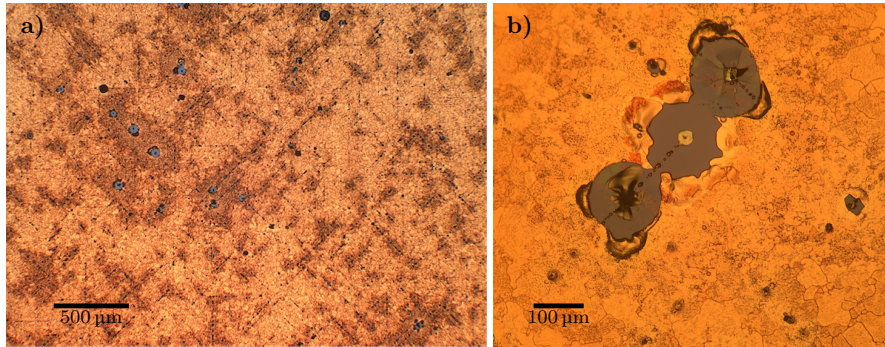


Figure 4.17: *Optical microscope images of Cu film surface after a CVD process with the Cu substrate only supported by two extremities making it more prone to buckling under its own weight.*

4.3 Role of surface confinement

4.3.1 Confinement as observed

The various experimental results presented in the preceding sections suggest that confining the Cu surface is a powerful and versatile tool to improve the synthesis of graphene. This section aims at reviewing the numerous mechanisms that are involved when using Cu surface confinement and describes how it favors the synthesis of high-quality graphene.

Suppression of Cu evaporation loss

Placing a flat and smooth inert material in close contact with the Cu vapor has been shown to efficiently trap the Cu vapor in the vicinity of the Cu surface. This vapor trapping establishes a quasi-static thermodynamic equilibrium between the solid and vapor phase of Cu which hinders further evaporation of the catalyst (as depicted in Fig. 4.18).

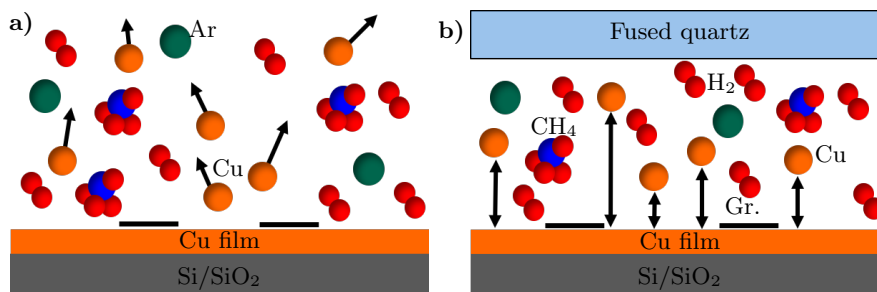


Figure 4.18: Schematic depiction of the influence of surface confinement on the evaporation of the Cu catalyst: a) strong Cu evaporation in absence of confinement. b) Cu vapor trapping and evaporation suppression using a quartz capping.

The suppression of evaporation loss is particularly interesting when growing graphene on thin Cu films as the evaporation loss leads to Cu film thinning, voiding, fingering, and solid-state dewetting eventually.

Cu surface confinement thus enables the growth of graphene on thin Cu film using a higher temperature ($T \leq 1050$ °C) and for a longer duration which is essential for achieving high-quality graphene.

Although the Si contamination is the major factor inhibiting the nucleation and growth of graphene on thin Cu film, it has also be found that graphene can only be grown at lower pressure ($P_{gr} \sim 0.5$ mbar) when the Cu surface is confined. As described in section 4.1, this phenomenon was also observed on Cu foil. It is thus believed that there exists a competition between the Cu evaporation and the graphene growth but the Cu evaporation is only detrimental for graphene nucleation at lower global pressure.

Improved CVD conditions at Cu surface

In addition to controlling the Cu vapor in the vicinity of the Cu surface, the Cu surface confinement also modifies the partial pressure of methane, hydrogen and argon. Indeed, due to the capping material deposited in close contact with the Cu surface, the transport of CH_4 and H_2 gas molecules is achieved through diffusion at the interface instead of gas convection in the atmosphere mainstream. Given that the gas phase diffusivity is higher for H_2 than for CH_4 and Ar molecules and given that the CH_4 molecules are consumed by the Cu surface to produce graphene and H_2 as a by-product, the partial pressure of CH_4 decreases while the partial pressure of H_2 increases with the distance from the Cu sample edges. The enhanced H_2 -to- CH_4 ratio and lowered CH_4 partial pressure present in the central region of the sample compared with the atmosphere in the CVD furnace is depicted in Fig. 4.19. Cu surface confinement is thus particularly interesting when the CVD setup cannot deliver optimal conditions such as a low partial pressure of methane and a high H_2 -to- CH_4 ratio which are known to improve graphene domain density, shape and structural quality.

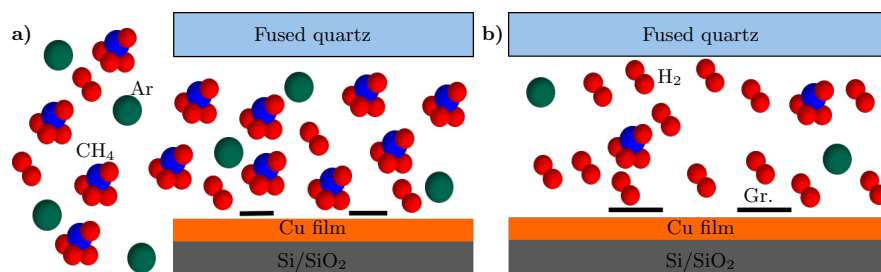


Figure 4.19: Schematic depiction of the influence of surface confinement on the composition of the atmosphere near the Cu surface (a) close to the Cu sample edge and (b) in the central region of the Cu sample.

Protection of Cu surface from undesired species

Cu surface confinement also prevents undesired gaseous species to reach the Cu surface and have a detrimental effect on the graphene growth. The capping material placed between the Cu surface and the CVD atmosphere prevents adventitious particles transported by the gas flow mainstream to be deposited on the Cu surface. The capping material also prevents the Cu catalyst to gather all the contaminants that have a strong affinity with it including carbonaceous gas molecules and ubiquitous silicon. The contamination can have various impacts on the synthesis of graphene. Some particles can be deposited on the Cu surface and act as parasitic active sites for nucleation. Carbonaceous species resulting from the pyrolysis of adventitious polymeric residues inside the CVD furnace during the warming step can be transported through the CVD chamber and cracked on the Cu surface similarly to methane. This phenomenon increases the carbon concentration of the Cu surface prior to the graphene growth step and makes the catalyst more prone to produce unwanted additional graphene nuclei.

In order to reach the Cu surface, the undesired species have to diffuse along the interface. Owing to the small spacing between the Cu and the quartz surfaces, these species have a finite diffusion length and can only

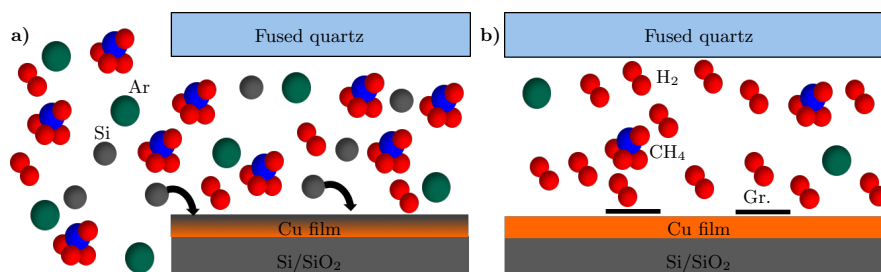


Figure 4.20: Schematic depiction of the role of Cu surface confinement in reducing the arrival of undesired species that can adversely impact the growth of graphene. a) Edge of the Cu sample which is exposed to all sorts of undesired species present in the CVD atmosphere. b) Purified atmosphere in the vicinity of the Cu surface in the central region of the catalyst owing to the finite diffusion length of the undesired gas molecules.

interfere with the graphene growth on the Cu sample periphery. The protection of undesired species is even more important when it prevents the Cu catalyst poisoning from silicon as schematically represented in Fig. 4.20.

Better reproducibility

The quartz cap protects the Cu surface from gas flow non-uniformities or turbulences that are inherent to any CVD systems and difficult to control, measure and predict. Tuning the surface confinement by adjusting the spacing of the interface or the size of the sample makes the graphene deposition more controllable and can lead to improved graphene uniformity.

4.3.2 Confinement in the literature

The results presented in this chapter have been found back in 2013-2014. At that point, very few research groups reported that the graphene growth could be improved by avoiding, in one way or another, the direct exposure of the Cu surface from the CVD gas mainstream.

In this respect, Li *et al.* [105] were the first to report improved graphene growth results using a particular Cu foil geometry. By bending a Cu foil in two and then crimping the three remaining sides, they obtained a Cu foil enclosure (also called "pocket") that has been loaded in the CVD furnace. Although graphene was produced inside and outside the enclosure, the inner surface was exhibiting a lower graphene domain density that could reach a lateral size of about 0.5 mm after extended periods of time (≥ 1 h). The improved graphene results were attributed to a lower partial pressure of methane, the Cu vapor in static equilibrium and a potentially lower pressure of unwanted species in their non-UHV system. They however did not provide any concrete evidence supporting their claims.

One year later, in 2012, Zhang *et al.* [124] rolled up a Cu foil and placed it into a quartz tube with only one open end (also called "cuvette"). This cuvette was then placed into the CVD furnace with the open end facing the CVD furnace gas inlet. They observed that placing the Cu foil inside the cuvette was yielding large flower-shaped graphene domains with lateral size reaching 100 μm while placing the Cu foil outside was leading to a continuous graphene film with slight etching. They believed that the gases that were flowing into the tube get trapped inside, thus leading to a gas composition and gas flow rate different from outside the cuvette. More particularly, they believe that the vapor trapping effect of the cuvette reduces the carbon supply and creates a quasi-static reactant gas distribution.

In 2013, Chen *et al.* [107] also employed different Cu foil geometries by rolling up the foils into long narrow tubes (5 cm-long with a 5 mm diameter) or stacking them on top of each other. They demonstrated that these geometries were able to produce graphene domains reaching a lateral size of about 1.9 mm. The low nucleation site density required

to achieve such a result was, according to the authors, exclusively attributed to the evaporation and re-deposition of Cu atoms on the inner side of the Cu tube that was making the inner Cu surface about 10 times smoother than the outer one.

Although these three pioneering papers did not provide a comprehensive explanation about the physical mechanisms that contributed to improve the graphene growth results, they aroused considerable interest among the scientific community.

Cu foil pockets and other geometries: Jacobberger *et al.* [88] used Cu foils pockets to enclose their epitaxial Cu films on which they wanted to grow graphene as they argue it offers unique advantages including (i) the steady-state supply of Cu vapor from the Cu foil to the Cu film, thus reducing morphological evolution of the Cu film upon exposure to high-temperature low pressure conditions over long periods of time, (ii) the reduction of SiO₂ particles deposited on the catalytic surface that are believed to originate from the quartz tube and that can act as preferential sites for nucleation, and (iii) the tortuous paths that the precursors have to diffuse through in order to enter the Cu foil decreases the precursors partial pressure and thus reduces the nucleation site density.

Similarly, Miseikis *et al.* [106] ascribed the reduction of nuclei density to a lower precursor impingement flux inside the Cu foil enclosure. In contrast, Hsieh *et al.* [180] believed that the main role of the enclosure lies in improving the Cu surface roughness.

In a different vein, Hsieh *et al.* [181] conducted the growth of graphene on a close-packed stack of gapless and alternating layers of graphite and Cu, aiming to achieve a high-throughput production. Although they did not obtained large graphene crystals, they observed a 10-fold decrease of the nucleation site density in confined Cu surfaces compared with non-confined Cu foils. They attributed this observation to the reduction of precursor concentration below the critical threshold of adsorption-controlled nucleation kinetics. They also observed that the nucleation site density remains relatively constant over the confined Cu foil surface

while the domain size is significantly smaller in the center of the confined sample. They explained these observations by the fact that the growth process is controlled by the arrival of methane which takes place through diffusion at the interface and which is impeded in the sample center.

Quartz cuvettes and restricted reaction chambers: Rummeli *et al.* [109] observed that placing the Cu foil inside quartz cuvettes (with the open end facing the gas exhaust of the CVD furnace) was contributing to the homogenization of the graphene film number of layers. This observation was explained by the fact that methane molecules have to surround the cuvette in order to gently diffuse inside and reach the Cu foil. This elongated path leads to fewer active species on the Cu surface and thus lowers the chances of forming bilayers. Other research groups also employed backward faced quartz cuvettes [110, 111]. Wang *et al.* [110] employed a 40-cm-long cuvette and attributed the ultra low nucleation site density obtained near the close end of the cuvette (~ 10 nuclei/cm²) to the significant reduction of the gas flow velocity along the Cu surface (by about 5 orders of magnitude). Song *et al.* [111] showed that the "vapor blocking effect" induced by the cuvette leads to a re-distribution of the gas flow field and significantly enhances the H₂-to-CH₄ ratio. Their computational fluid dynamics (CFD) simulations pointed out that the gas convection inside the cuvette is suppressed and given that the diffusivity of CH₄ is lower than the one of H₂, the cuvette has a higher H₂-to-CH₄ ratio and a lower partial pressure of CH₄.

Instead of using hand-made Cu foil complex geometries or using relatively large cuvettes that only induce a shallow confinement effect, a few research groups employed customized mountings that could support the Cu foil and create a confined reaction space [112, 182, 183]. Cho *et al.* [182] built up an alumina "jig" in which the gap between the lower plate and the upper lid can be adjusted between 100 μ m and several millimeters. When the gas stream flows through the gap, the various gas species reach the Cu foil *via* molecular diffusion instead of convection. They observed that the jig was limiting the degradation of the Cu surface morphology induced by the strong Cu sublimation during the Cu annealing step but they however did not observe an impact on the nucle-

ation site density. Chen *et al.* [112] devised a confined reaction space in which the Cu foil is sandwiched between a pair of quartz slides separated by a 50- μm -thick U-shape tungsten spacer with the gas inlet oriented toward the gas outlet of the CVD furnace. They pointed out that using a confined reaction space hinders the gas-phase transportation of C precursors on the catalyst surface thus making the graphene growth kinetics shift toward a mass-transport-limited regime which tends to make the growing front of graphene domain more dendritic.

Confinement using Cu films: Lee *et al.* [139] reported that covering the Cu film during the CVD protocol contributes to reducing the Cu evaporation loss induced by the exposure to high temperature/vacuum environment, and thus enables the high-temperature annealing of the Cu film for more than 4 hours without severe damages. They also found that the Cu grain evolution saturates after a 60-min long annealing step and the graphene domain size is independent of the underlying Cu grain size. Lester *et al.* [184] also observed that confining the Cu film surface was lessening the loss of Cu during the CVD process and thus preventing the walls of their cold-wall CVD setup to be coated with Cu.

Cu foil backside-induced confinement: Very recently, Wang *et al.* [114] showed that the nucleation site density on the Cu foil backside was better than the one on the Cu foil topside. They annealed the Cu foils under a non-reducing atmosphere in order to maintain the Cu native oxide layer on the Cu foil surface and thus to benefit from the role of oxygen in decreasing the nucleation site density (which is discussed in chapter 7). The better nucleation density obtained on the Cu foil backside was attributed to the confinement-induced trapping effect that prevents oxygen from escaping the surface and thus stays for a longer period of time in the vicinity of the Cu surface.

4.3.3 Discussion

The aforementioned papers agree in one way or another that avoiding the direct exposure of the Cu substrate improves the growth of graphene. Cuvettes have been found to locally reduce the velocity of gas species flowing along the Cu substrate and locally reduce the C precursor concentration. Cu enclosures, stacks, rolls or confined reaction space not only result in quasi-static CVD conditions but they appear to be more efficient to trap Cu vapor and establish a quasi-static equilibrium between the gas-phase and the solid phase of Cu, thus preventing Cu loss and contributing to smoothen the surface. There are however some discrepancies concerning the impact of confinement on the nucleation site density, the graphene growth rate or the graphene growth front morphology.

Obtaining a lower C precursor concentration in the gas phase, suppressing the Cu evaporation and slowing down the gas flow stream can however be achieved at the CVD reactor scale by diluting the methane flow rate, performing the CVD growth under higher global pressure levels, and reducing the global flow rate, respectively. Nevertheless, these CVD parameters have not been able to successfully produce graphene with equivalent quality as obtained with Cu surface confinement, evidencing that our understanding of the involved graphene growth mechanisms remains quite limited.

The lack of understanding mainly arises from the wide variety of CVD procedures that have been reported including (i) different Cu pre-growth treatments, (ii) mainstream CVD conditions, and (iii) various approaches employed to achieve the confinement. Especially, the arbitrariness of the hand-made Cu foil geometries results in a non-reproducible local environment as the blocking effect of gas species diffusing in (H_2 , CH_4 , Ar) or out (Cu vapor) the enclosure varies from one process to another. Moreover, it has been discovered that active C species adsorbed on the Cu surface could diffuse through the Cu foil thickness and contribute to graphene nucleation and growth on the other side which makes the growth mechanisms inside Cu enclosures, tubes and stacks more complex to study (see ref. [185] and chapter 7).

It is truly believed that Cu films can be of great interest for systematically investigating the exact role of Cu surface confinement. The smooth, flat and rigid catalytic substrate can be used to obtain a constant gap over a long range, thus better controlling the extent of the surface confinement. Cu samples can also be held vertically in the horizontal CVD furnace which makes them oriented perpendicularly to the gas flow and thus reduces convection effects. Moreover, using a Cu film evaporated on a quartz substrate suppresses the contribution of C species that are generated on the other side and capable of diffusing through the catalytic substrate thickness as it is the case for Cu foils. It is also worth mentioning that rigorously investigating the impact of Cu surface confinement on the graphene domain morphology requires a sufficiently low nucleation site density. Indeed, large domains must be grown in order to observe the instabilities of the growth front which only really appear for domain sizes exceeding several tens of microns.

4.4 Conclusions

The preliminary CVD experimental campaign described in this chapter has been helpful to observe a series of original growth behaviors and to better understand the complex CVD mechanisms governing the growth of graphene.

First, it is found that growing graphene on thin Cu films is more complex than on widely spread Cu foils. The main difficulty lies in achieving appropriate CVD conditions while maintaining the Cu film physical integrity and avoiding the Cu catalyst poisoning. The Cu film integrity can be maintained by either adapting the CVD protocol, increasing the Cu film thickness or by exploiting the Cu surface confinement.

Second, it is found that Cu surface confinement is a powerful tool to improve the graphene growth results. This Cu surface confinement that has been mainly studied using thin Cu films is very likely to be responsible for the better graphene results obtained at the Cu foil backside compared with the Cu foil topside which is directly exposed to the CVD furnace atmosphere.

Finally, it has been found that using silicon wafers represents a high degree of contamination risk for the CVD furnace. Using an entire 3-inch Cu/SiO₂/Si/SiO₂ for every single CVD experiment does not represent a viable approach given that their fabrication is time, resource and energy consuming, cumbersome and involves a great deal of money. Moreover, the pre-CVD processing of Cu film substrates (for instance, to deposit or pattern the Cu film) is rather limited as any process step could potentially damage the thin SiO₂ coating that protects the CVD atmosphere from the silicon. Moreover, the contamination induced by the CVD processing of one defective Cu film substrate can alter the graphene growth of subsequent CVD experiments, which is detrimental to the repeatability and reproducibility of the CVD processes.

These findings provide a series of guidelines that are of central importance for further improving the CVD process:

1. Catalytic substrate

Given that the Cu film represents a more attractive catalytic substrate than the Cu foil, it has been decided to further investigate the growth of graphene on thin Cu films. However, the thermally oxidized silicon wafer is replaced by a fused quartz wafer which is resistant to high temperature processes, chemically inert and can be cleaved in small pieces (as explained in chapters 3). Moreover, as explained later in this thesis (see chapters 6 and 7), it is essential to expose the Cu catalyst to high temperatures for both the Cu annealing and graphene growth steps in order to obtain millimeter-size graphene domains. In order to maintain the physical integrity of the Cu film upon the CVD process, it will be thus preferred to increase the Cu film thickness rather than minimizing the exposure to high temperature.

2. CVD conditions

The better graphene growth results achieved using Cu surface confinement are mainly attributed to better CVD conditions locally generated in the vicinity of the Cu surface. Unfortunately, the Cu surface confinement reduces the scalability of the CVD process. Although the Cu surface confinement has been proven to be beneficial for the graphene growth on 3-inch wafers, it is probably not the case for larger samples or other CVD conditions. Improving the conditions present in the CVD atmosphere and not only in the vicinity of the Cu surface is crucial for the development of a scalable process. As a consequence, the main focus of future efforts have been dedicated to modify the CVD equipment in order to obtain higher H_2 -to- CH_4 ratio and lower P_{CH_4} inside the CVD furnace. The various modifications made to the CVD equipment, along with their potential impact on the CVD conditions are described in chapters 5.

Chapter 5

CVD Equipment Customization

As aforementioned in chapter 2, graphene domain size, density and number of layers strongly depends on the CVD conditions employed during the graphene growth step. In chapter 4, various combinations of CVD parameters including the global pressure (P_{gr}), growth temperature (T_{gr}), gas flows of methane (F_{CH_4}) and hydrogen (F_{H_2}) have been investigated in order to elaborate a "CVD recipe" yielding high-quality single-layer graphene.

Chapter 4 demonstrated that even under the best conditions that could be achieved with the initial CVD setup, the graphene growth results were very poor compared to what was reported in the literature. The only decent graphene growth results were obtained using Cu surface confinement that is believed to locally enhance the hydrogen-to-methane ratio (R) and reduce the partial pressure of methane (P_{CH_4}).

Instead of improving the growth conditions locally in the vicinity of the Cu surface using particular Cu substrate configurations, improving the gas flow mainstream composition represents a more viable and desirable route for industrial production. This chapter describes step-by-step the successive modifications that have been made to the initial CVD setup and how these modifications impacted the CVD parameter space. Unlike chapters 4, 6 and 7 that aim at better understanding the graphene growth mechanisms and improving graphene quality by taking into ac-

count scientific and technological considerations, this chapter focuses on improving the growth of graphene using more technical considerations.

5.1 Initial CVD setup

As a reminder, in the first stage of the CVD parameters investigation, T_{gr} was set to 1000 °C which is an intermediate temperature between the threshold temperature for graphene growth on Cu using methane (~ 840 °C) and the Cu melting temperature (~ 1084 °C). Although increasing the temperature yields better graphene results in terms of nucleation site density and number of layers, it also contributes to damage the Cu substrate through evaporation loss. The LPCVD setup was not designed to properly control the global pressure inside the furnace and P_{gr} could only be adjusted in the 0.5-2 mbar range using the throttle valve.

When seeking optimal values for P_{CH_4} and H_2 -to- CH_4 ratio and trying to understand their role in graphene growth, it has been observed that the best results were achieved when the methane flow rate was set to its minimum (5 sccm), and the hydrogen flow rate was set to its maximum (65 sccm). Although the mass flow controller (MFC) is able to deliver an even lower methane flow rate, this value corresponds to 5% of the MFC's full scale and represents a reasonable lower limit in order to have reproducible and repeatable experiments. Using a higher hydrogen flow rate would have been beneficial for graphene growth but the pumping system can only tolerate a total gas flow rate of about 70 sccm. Unfortunately, even under optimal conditions, as-produced graphene domains were exhibiting a dendritic shape and lateral dimensions inferior to a dozen of micrometers as shown in Fig. 5.1.

These poor initial synthesis results suggested that the CVD system had rather limited capabilities. Table 5.1 displays the H_2 -to- CH_4 ratios and methane concentration (C_{CH_4}) and P_{CH_4} in the worst and best case scenarios that could be reached with the initial CVD setup. These conditions are calculated using the general equations:

$$P_{CH_4} = P_{tot} \times \frac{F_{Ar/CH_4} \times D_{CH_4}}{F_{Ar/CH_4} + F_{Ar/H_2}}, \quad (5.1)$$

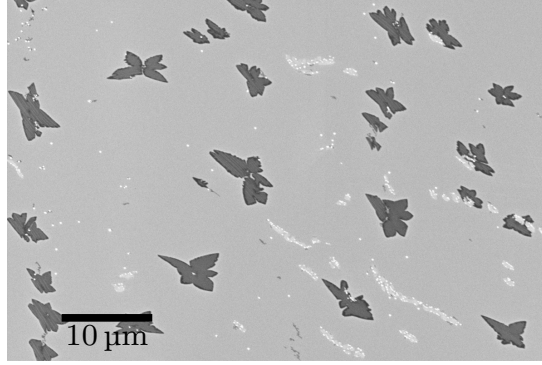


Figure 5.1: *In-lens SEM image of graphene domains as-grown on the Cu foil backside using the initial CVD equipment.*

$$C_{CH_4} = \frac{P_{CH_4}}{P_{tot}} = \frac{F_{Ar/CH_4} \times D_{CH_4}}{F_{Ar/CH_4} + F_{Ar/H_2}}, \quad (5.2)$$

$$R = \frac{F_{Ar/H_2} \times D_{H_2}}{F_{Ar/CH_4} \times D_{CH_4}}. \quad (5.3)$$

D_{CH_4} and D_{H_2} are respectively the dilutions of the CH_4 and H_2 gas feedstocks. Initially, $D_{CH_4}=100\%$ and $D_{H_2}=5\%$. The P_{CH_4} equation does not take into account the third gas line containing pure argon feedstock as adding a pure Ar flow will have a detrimental impact on the H_2 -to- CH_4 ratio given the constraint about the global pressure that cannot exceed 70 sccm.

Again, for reproducibility and repeatability concerns, the lowest Ar/ H_2 gas flow rate that has been used during the CVD parameters investigation is set to 10 sccm which corresponds to 5% of the full scale of the MFC. Comparing the parameter space that can be achieved with the initial CVD setup with those reported in literature (see tables in chapter 2) reveals that the setup has to be modified in order to reach higher H_2 -to- CH_4 ratios and lower C_{CH_4} . The following sections describe the various adjustments that have been made to the CVD setup and how they impacted the CVD parameter space.

Table 5.1: Summary the CVD conditions achieved in the best and worst case scenarios with the initial CVD equipment. The best results have been obtained with $P_{gr}=0.5$ mbar while the worst results have been obtained with $P_{gr}=2$ mbar.

	Gas flows	H_2/CH_4	C_{CH_4}	P_{CH_4} [mbar]
Best	$F_{CH_4}=5$ sccm $F_{Ar/H_2}=65$ sccm	~ 0.65	$\sim 7.1 \times 10^{-2}$	$\sim 3.6 \times 10^{-2}$
Worst	$F_{CH_4}=60$ sccm $F_{Ar/H_2}=10$ sccm	$\sim 8.3 \times 10^{-3}$	~ 0.86	~ 1.7

5.2 Increasing H_2 concentration

The first modification concerns the dilution of the Ar/H_2 gas feedstock that has been raised from 5 % to 10%. Maintaining a relatively low concentration of hydrogen is preferable knowing that its lower explosive limit (LEL) is $\sim 4\%$ in air. A concentration of 10% represents a reasonable amount of hydrogen that meets the safety requirements in case of leakage during the high temperature CVD process. As shown in table 5.2, the two-fold increase of D_{H_2} improves the H_2 -to- CH_4 ratio but does not impact methane partial pressure or concentration.

Table 5.2: Summary of the CVD conditions achieved in the best and worst case scenarios after increasing the H_2 feedstock concentration from 5% to 10 %.

	Gas flows	H_2/CH_4	C_{CH_4}	P_{CH_4} [mbar]
Best	$F_{CH_4}=5$ sccm $F_{Ar/H_2}=65$ sccm	~ 1.3	$\sim 7.1 \times 10^{-2}$	$\sim 3.6 \times 10^{-2}$
Worst	$F_{CH_4}=60$ sccm $F_{Ar/H_2}=10$ sccm	$\sim 1.7 \times 10^{-2}$	~ 0.86	~ 1.7

5.3 Diluting CH₄ gas feedstock

In order to reach a higher H₂-to-CH₄ ratio and a lower P_{CH₄}, the methane gas feedstock has been diluted in argon with a concentration of 10%. Even though the H₂-to-CH₄ ratio can be set to values 20 times higher than initially, the best graphene growth results in terms of domain shape and size are still obtained using the lowest amount of methane and largest amount of hydrogen that can be delivered by the MFCs while avoiding the pump to shut down (see table 5.3). Figure 5.2 shows that graphene domains produced with a H₂-to-CH₄ ratio of 13 still present a strong dendritic growth behavior.

Table 5.3: *Summary of the CVD conditions achieved in the best and worst case scenarios after decreasing the CH₄ feedstock concentration from 100% to 10%.*

	Gas flows	H ₂ /CH ₄	C _{CH₄}	P _{CH₄} [mbar]
Best	F _{Ar/CH₄} =5 sccm F _{Ar/H₂} =65 sccm	~ 13	~ 7.1 × 10 ⁻³	~ 3.6 × 10 ⁻³
Worst	F _{Ar/CH₄} =60 sccm F _{Ar/H₂} =10 sccm	~ 0.17	~ 8.6 × 10 ⁻²	~ 0.17

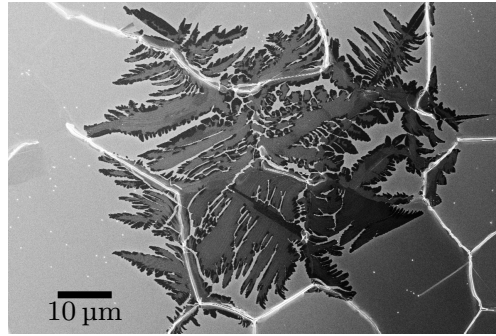


Figure 5.2: *In-lens SEM image of graphene domains as-grown on the Cu foil backside using a H₂-to-CH₄ ratio of about 13 and a pressure of about 1 mbar.*

5.4 Changing the pumping system and switching the MFCs

In order to further increase the amount of hydrogen and further dilute the methane in the gas phase of the CVD furnace, the turbo molecular pump has been replaced by a dry Scroll pump (Oerlikon Leybold Vacuum, ScrollVac SC-15D). This kind of pump has been mainly chosen as it is relatively cheap (4094 euros excl. VAT), can tolerate a higher gas flow throughput and does not contain any oil. Avoiding oil is critical when producing graphene as any oil residues that would be transported upstream would undergo pyrolysis in the furnace and adversely impact the repeatability and reproducibility of the experiments. Even though scroll pumps generally exhibit a poor ultimate vacuum (2×10^{-2} mbar) compared with the turbo-molecular pump (2×10^{-5} mbar), it does not impede the proper functioning of the CVD process. Indeed, pressures below 10^{-1} mbar could only be reached when using a small total gas flow (which prevents having a high H_2/CH_4 ratio) and would be causing an excessive Cu sublimation upon the CVD process which is particularly detrimental to the Cu film physical integrity.

As the pump can tolerate a larger total gas flow rate, the MFCs of Ar and Ar/H_2 have been switched in order to be able to introduce an hydrogen flow rate up to 500 sccm. Yet again, the best graphene growth results were obtained when employing the CVD conditions at the limits of the capabilities of the setup as shown in table 5.4.

Table 5.4: *Summary of the CVD conditions achieved in the best and worst case scenarios after replacing the turbo pump by a scroll pump and switching the MFCs.*

	Gas flows	H_2/CH_4	C_{CH_4}	P_{CH_4} [mbar]
Best	$F_{Ar/CH_4}=5$ sccm $F_{Ar/H_2}=500$ sccm	~ 100	$\sim 9.9 \times 10^{-4}$	$\sim 5 \times 10^{-4}$
Worst	$F_{Ar/CH_4}=100$ sccm $F_{Ar/H_2}=25$ sccm	~ 0.25	$\sim 8 \times 10^{-2}$	~ 0.16

5.5 Turbo-molecular pump for cleaning purposes

Although the turbo-molecular pump has been replaced, it has not been thrown away but placed in parallel with the scroll pump in order to be able to exploit it when a lower global pressure needs to be established in the CVD furnace (see Fig. 5.3). Reaching a low pressure is particularly interesting for cleaning the substrate support, the inner walls of the CVD furnace and the thermoblocks that accumulate Cu condensates and undesired graphene. Indeed, through each CVD process, the Cu catalyst evaporates and re-deposits inside the CVD furnace, most likely on the inner wall of the CVD furnace due to the presence of temperature gradients.

As explained later in chapter 6, the modification of the cleanliness of the furnace can impact the growth of graphene. It is thus preferable to proceed to the cleaning of the equipment once in a while.

The cleaning process can be either performed using chemicals or by physical evaporation/desorption/etching. Using successive baths of HCl/H₂O₂, H₂SO₄/H₂O₂ (known as Piranha solution) and HF/H₂O mixtures is the most effective way to etch away the stacks of Cu/graphene sporadically deposited inside the quartz tube. However, this cleaning approach is not very convenient given that (i) it requires particular precautions while handling hazardous chemicals with the cumbersome 1.2-m-long quartz tube, (ii) it requires to de-assemble and re-assemble the flanges which is a time consuming and tedious task, (iii) it is not an eco-friendly process given the chemicals and the amount of de-ionized water employed and, (iv) it requires a long-duration high temperature dummy CVD process afterwards in order to anneal and evaporate residuals of chemicals. The second approach to clean the CVD furnace consists of heating the CVD furnace under a high temperature (≥ 1080 °C) and low pressure ($\leq 10^{-2}$ mbar) under a Ar/H₂ gas flow for a few hours in order to etch away the deposited graphene and carry away the vaporized Cu. Although this approach is time and energy consuming, it is preferred over the wet cleaning process.

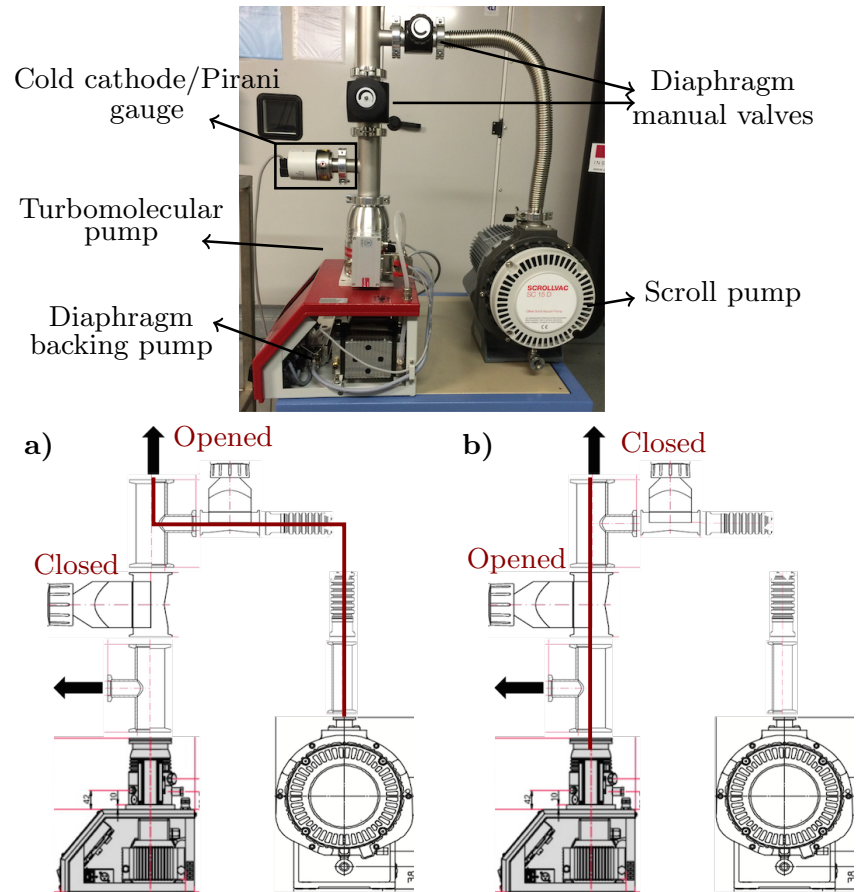


Figure 5.3: Photograph of the pumping system consisting of the scroll pump mounted in parallel with the turbo-molecular pump. The two manual diaphragm valves can be opened or closed depending on whether (a) the CVD growth or (b) the CVD furnace cleaning is running.

5.6 Adding a pressure control system

The new configuration of MFCs along with the scroll pump have extended the range of total gas flow that can be introduced in the CVD furnace ($500+100=600$ sccm instead of 70 sccm). Extending the total gas flow range results in the broadening of the global pressure range that can be established in the furnace during the CVD process. For instance, tuning the total gas flow rate from 30 to 600 sccm can lead to an increase of global pressure from 0.5 to 20 mbar while using the same throttle valve aperture.

Unfortunately, the throttle valve is not suitable to precisely control the global pressure inside the CVD furnace within the total gas flow rate range. The coupling between the gas flow rate and the global pressure reduces the parameter space and makes it more challenging to extract the optimal conditions for the growth of graphene. To address this issue, the CVD setup has been further customized by placing a pressure control system between the CVD furnace and the pumping system. This system, especially devised for the CVD furnace, consists of a rough diaphragm valve (Pfeiffer vacuum, DN 40 ISO-KF) placed in parallel with 2 fine metering valves (Pfeiffer vacuum, EVN 116, Gas dosing and shut-off valve, DN 16 ISO-KF) as shown in Fig. 5.4a.

The rough valve is of primary use when purging the tube prior to any CVD process (see configuration in Fig. 5.4c). Having a wide aperture and straight pipes ensure that the pressure inside the CVD furnace reaches a pressure level close to the ultimate vacuum of the pump within a reasonable timeframe. The 2 metering valves are of particular interest during the CVD synthesis protocol. These valves can be switched OFF or ON and the apertures can be precisely adjusted using the rotary knob. The interest of using two metering valves lies in the possibility of controlling the global pressure of the Cu annealing step with one valve and the one of graphene growth step with the second valve independently (see Fig. 5.4b). Using one single metering valve would require the manual adjustment of its aperture between the Cu annealing and the

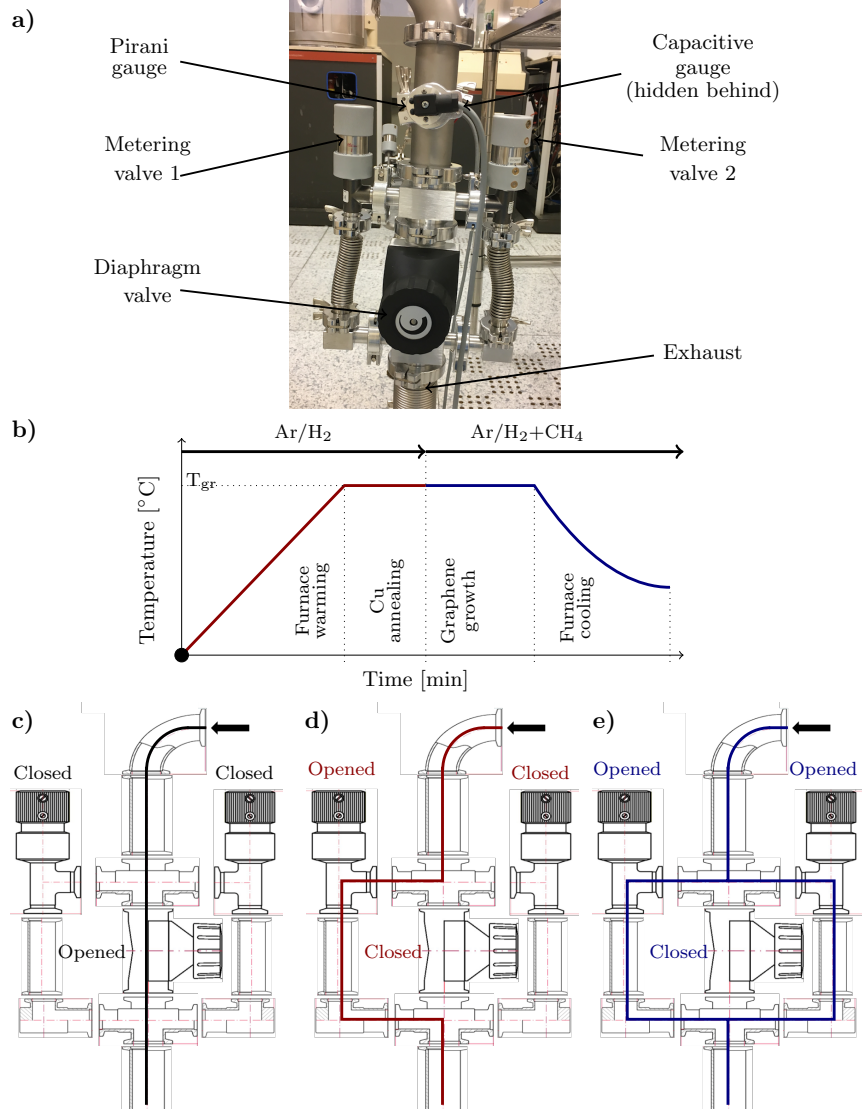


Figure 5.4: a) Photograph of the pressure control system. b) Typical CVD protocol temperature and gas flow profiles. The black dot in $t=0$ corresponds to the CVD furnace purge achieved by opening the rough diaphragm valve as shown in (c). The red and blue temperature profile corresponds to the valve configurations depicted in (d) and (e), respectively.

graphene growth step as the desired global pressure and the total gas flow rates employed for both steps most likely differ. As a consequence, the conditions in the CVD process would thus depend on the rate at which the aperture is adjusted and consequently on the dexterity of the CVD setup operator. In contrast, using two distinct valves allows the operator to preset their apertures before starting the CVD protocol and simply switch them from ON- to OFF-modes and vice versa during the CVD process as depicted in Fig. 5.4b-e.

Thanks to the pressure control system, the pressure inside the CVD furnace can be adjusted from 0.1 mbar up to near atmospheric pressure. The pressure is determined by the total gas flow introduced in the CVD furnace and the size of the aperture. Injecting gases in the furnace raises the pressure until it reaches an equilibrium between the gas flow injected and the gas flow passing through the aperture of one or more valves. It is interesting to note that the pressure reaches an equilibrium because the gas density going through the aperture increases with the global pressure while the flow velocity remains relatively close to the speed of sound (~ 343 m/s).

5.7 Replacing the pressure gauge

After a few trials, it was observed that the pressure inside the CVD furnace was strongly affected by the composition of the gas phase. For a given valve aperture and a total gas flow, the pressure reader was displaying two different pressure levels depending whether pure Ar, Ar/H₂ or Ar/CH₄ gases were employed. The pressure difference was getting more pronounced as the global pressure was rising.

After checking out the gauge specifications, it appeared that Pirani gauges are unsuitable for measuring the pressure of a gas phase mainly composed of argon for pressures exceeding 1 mbar. It has thus been decided to replace the hybrid Pirani/cold cathode gauge by a set of 2 independent gauges composed of a Pirani gauge (Pfeiffer Vacuum, TPR270)

and a capacitive gauge (Pfeiffer Vacuum, gas-independent transmitter CMR361). The Pirani gauge remains of interest when purging the furnace prior to starting the synthesis process. Pumping the CVD furnace down to the ultimate pressure of the pump is useful to get rid of potential undesired gaseous species and to verify that the furnace is hermetically sealed. On the other hand, the capacitive gauge ensures the precise measurement of the pressure in the 0.1-1100 mbar range, independently on the gas-phase composition.

Using this customized CVD setup, graphene growth experiments can be performed under either a low, an ambient or an intermediate pressure regime. As shown in chapter 2, the literature reported the synthesis of millimeter-size graphene domains under different pressure regimes. The scientific community did not reach a consensus concerning the pressure regime that would yield the best graphene results. Now that the pressure level can be precisely tuned over a broader range (0.1 to 1000 mbar instead of 0.5 to 2 mbar), the best results are no more obtained by simply using the conditions minimizing the partial pressure of methane. It appeared that maximizing the H_2 -to- CH_4 ratio is still a key strategy to obtain the best results in terms of graphene domain shape and density but tuning the global pressure regime over the entire range leads to various results from almost no graphene formation under a global pressure of 0.5 mbar to an excessively high density of graphene domain for CVD runs performed at a pressure exceeding 50 mbar.

When the global pressure was limited to the 0.5-2 mbar range, the best and worst case scenarios for the graphene growth were perfectly matching with the limits of the parameter space in terms of P_{CH_4} and H_2 -to- CH_4 ratio. Now that the global pressure represents a critical parameter to take into account, the optimal CVD conditions are more challenging to determine (see chapter 6). For the following sections, the tables summarizing the attainable CVD conditions are no longer organized as best and worst case scenarios for graphene growth but rather as lower and upper limits that can be achieved for the H_2 -to- CH_4 ratio (see table 5.5).

Table 5.5: Summary of the CVD conditions that can be achieved with the CVD setup after adding a pressure-control system. LP and AP refer to global pressures of 0.5 and 1000 mbar, respectively.

	Lower limit	Upper limit
Gas flows	$F_{Ar/CH_4}=100$ sccm $F_{Ar/H_2}=25$ sccm	$F_{Ar/CH_4}=5$ sccm $F_{Ar/H_2}=500$ sccm
H_2/CH_4	~ 0.25	~ 100
C_{CH_4}	$\sim 8 \times 10^{-2}$	$\sim 9.9 \times 10^{-4}$
P_{CH_4}	LP: $\sim 4 \times 10^{-2}$ mbar AP: ~ 80 mbar	LP: $\sim 5 \times 10^{-4}$ mbar AP: ~ 0.99 mbar

5.8 Further diluting CH₄ gas feedstock

Yet again, testing various combinations of H₂-to-CH₄ ratios, P_{CH_4} and P_{gr} did not yield similar nucleation site densities to what have been demonstrated in the literature. However, it is found that, for a given H₂-to-CH₄ ratio, the compactness of as-produced graphene domains can be significantly improved by performing the graphene growth step at a higher pressure level. Unfortunately, it was observed that raising the pressure also drastically increases graphene growth rate and adversely impacts the nucleation site density. As a consequence, the growth of a continuous graphene was completed within 15 minutes and it was becoming difficult to observe isolated graphene domains at graphene growth pressure levels beyond 50 mbar.

The high graphene growth rate and the poor nucleation site density suggest that an excessive amount of C active species are adsorbed on the catalytic surface. This is not surprising given that raising the pressure level while maintaining the same methane concentration results in an increase of the methane partial pressure in the gas phase. In other words, compared with the LPCVD process, performing the CVD growth under ambient conditions (1000 mbar) results in a 1000-fold increase of P_{CH_4} for a given H₂-to-CH₄ ratio.

As it is challenging to study graphene growth at pressure levels superior to 50 mbar, the parameter space that can be investigated is rather limited and the potential of the newly designed CVD setup cannot be fully realized. It has thus been decided to further dilute the methane gas feedstock from 10% down to 2% in argon. After carrying out many experiments, it appeared that raising the global pressure from 50 mbar to 750 mbar was producing graphene domains with hexagonal shapes and smooth edges. Nevertheless, the best nucleation site density results were once again achieved using the limits of the MFC's capabilities (that is, 5 sccm of Ar/CH₄ and 500 sccm of Ar/H₂). It has thus been decided to even more dilute the methane gas feedstock down to 0.25% (as employed in chapter 6) and eventually down to 0.2% (as employed in chapter 7). As shown in table 5.6, employing an Ar/CH₄ (2000 ppm) mixture as methane feedstock enables the equipment to tune the H₂-to-CH₄ ratio in the 12.5-5000 range which thus covers most of the experimental conditions that have been reported so far in the literature (see tables in chapter 2).

Using such a highly diluted methane gas feedstock is particularly interesting as the best results are no more achieved when pushing the CVD setup to its limits. This dilution level has been determined in order to have best graphene growth results (on both Cu foils and Cu films) using a methane gas flow in the 20-50 sccm range for reproducibility and repeatability concerns, and a hydrogen gas flow ranging from 300 to 400 sccm (instead of 500) in order to extend the lifetime of the gas bottle.

Table 5.6: Summary of the CVD conditions that can be achieved with the CVD setup after all the modifications that have been aforementioned. $C_{CH_4} = 2000$ ppm ($=0.2$ %). LP and AP refer to global pressures of 0.5 and 1000 mbar, respectively.

	Lower limit	Upper limit
Gas flows	$F_{Ar/CH_4} = 100$ sccm $F_{Ar/H_2} = 25$ sccm	$F_{Ar/CH_4} = 5$ sccm $F_{Ar/H_2} = 500$ sccm
H_2/CH_4	~ 12.5	~ 5000
C_{CH_4}	$\sim 1.6 \times 10^{-3}$	$\sim 2 \times 10^{-5}$
P_{CH_4}	LP: $\sim 8 \times 10^{-4}$ mbar AP: ~ 1.6 mbar	LP: $\sim 1 \times 10^{-5}$ mbar AP: $\sim 2 \times 10^{-2}$ mbar

5.9 Adding an oxygen line

As shown in chapter 6, the Ar gas feedstock contains oxygen residuals that, when injected inside the CVD furnace during the Cu annealing step, effectively contribute to reduce the nucleation site density of graphene. As the Ar feedstocks contains only a few ppm of O_2 , a higher pressure of Ar is necessary to achieve a significant improvement of the nucleation site density.

In order to rigorously study the role of oxygen on graphene growth, it is thus preferable to be able to precisely control the oxygen content without having to tune the global pressure. It has thus been decided to add a fourth gas line to the CVD setup that can deliver a controlled amount of oxygen to the furnace, independently from the global pressure.

To avoid any risk of explosion caused by the reaction of oxygen and hydrogen in a furnace, it is preferable to ensure that hydrogen and oxygen cannot be introduced in the CVD furnace simultaneously. To do so, the O_2 supply line has been connected to the same MFC as the H_2 supply line using a 3-way ball valve (Swagelok). This gas line configuration is particularly interesting as it allows the precise monitoring of the O_2 gas flow rate without purchasing an additional MFC.

Given the strong affinity of copper with oxygen, the initial gas feedstock was chosen to be a O_2/Ar (1%) gas mixture. After a series of experiments (see chapter 7), it has been found that it was difficult to control the oxidation level of Cu during the Cu annealing step. Using for instance an oxygen partial pressure (P_{O_2}) of about 10^{-2} mbar (obtained when only the Ar/O_2 MFC is open but the global pressure is kept at a low level (around 1 mbar)) results in irreversible and undesired modification of the Cu foil surface and strong solid-state dewetting of the Cu thin film. The Cu surface degradation is attributed to the over-oxidation of the catalytic substrate during the Cu annealing step and the subsequent reduction induced by the reducing atmosphere required to grow graphene.

Although the O_2 concentration of the CVD furnace atmosphere can be further decreased by reducing the O_2/Ar gas flow and injecting simultaneously an important flow of pure Ar, the O_2 concentration remains too high to be able to perform Cu annealing steps under near ambient pressure while fine-tuning the oxidation of the Cu foil (see table 5.7). As a consequence, the oxygen gas feedstock has been replaced by an Ar/O_2 0.05% (or 500 ppm, Praxair) gas mixture.

Table 5.7: *Summary of the oxygen partial pressure that can be obtained during the pre-growth CVD step (i.e. the Cu annealing step) as a function of the global pressure, the gas flows and the dilution level of the O_2 feedstock.*

Gas flow rates	$P_{\text{tot}} = 1$ mbar	$P_{\text{tot}} = 1000$ mbar
200 sccm (1% O_2)	~ 0.01 mbar	~ 10 mbar
25 sccm (1% Ar/O_2) + 500 sccm (pure Ar)	$\sim 4.8 \times 10^{-4}$ mbar	~ 0.48 mbar
200 sccm (500 ppm Ar/O_2)	$\sim 5 \times 10^{-4}$ mbar	~ 0.5 mbar
25 sccm (500 ppm Ar/O_2) + 500 sccm (pure Ar)	$\sim 2.4 \times 10^{-5}$ mbar	$\sim 2.4 \times 10^{-2}$ mbar

5.10 Replacing the MFCs

The last upgrade that has been made to the CVD equipment consists of replacing the three mass flow controllers. Although the previous MFCs were fulfilling their role, having new MFCs appeared to be necessary for the following reasons:

- 1. Better specifications:** The initial MFCs were relatively cheap and were exhibiting poor specifications. In contrast, the newly installed MFCs (Horiba, SEC-N100 series) have better specifications as shown in Table 5.8.
- 2. More appropriate full-scale range:** As shown in the chapters 4 and 6, precisely adjusting the P_{CH_4} is essential to achieve a low density of nucleation site. Fine-tuning P_{CH_4} requires to precisely control F_{CH_4} introduced in the CVD furnace. Using a MFC with a full scale of the same order of magnitude as the flow rate that is employed during the CVD process ensures a better accuracy.
- 3. Broader parameter space:** The newly installed MFCs have the particular feature that their full-scale can be adjusted (to a certain extent). The MFCs purchased for controlling the Ar and Ar/H₂ flow rates have a full scale of 1 slm (=1000 sccm) while the one dedicated to the Ar/CH₄ flow rate has a full scale of 100 sccm. The full scale of these MFCs can however be adjusted down to 30% of their initial full scale which gives them a higher accuracy and flexibility.

Better specifications and more appropriate full-scale ranges can further improve the graphene growth results and lead to more reproducible and repeatable experiments.

Table 5.8: *Comparison of the specifications of the MFCs initially present and newly installed in the CVD setup. S.P. and F.S. refer to the set point and the full scale, respectively.*

Specifications:	Sevenstar	Horiba
Accuracy	$\pm 1.5\%$ F.S.	$\pm 1.0\%$ S.P. (rate $\geq 30\%$ F.S.) $\pm 0.3\%$ S.P. (Rate $\leq 30\%$ F.S.)
Control range	5-100 % of F.S.	2-100 % of F.S.
Response time	1~3 second	≤ 1 second
Linearity	$\pm 1\%$ F.S.	$\leq \pm 0.5\%$ F.S.
Repeatability	$\pm 0.2\%$ F.S.	$\leq \pm 0.2\%$ F.S.

5.11 Discussions and conclusions

Many modifications have been made to the CVD setup in order to precisely explore a wider range of CVD conditions. These modifications have been elaborated in order to optimize the conditions for both, the Cu annealing and the graphene nucleation and growth steps. The extension of the scope of CVD condition is illustrated in Figure 5.5.

Such extension of the parameter space has been made possible by combining a few key elements:

- Appropriate gas feedstock dilutions
- Adequate MFC full scales
- Precise pressure control system
- Accurate pressure gauges

Figure 5.6 shows the evolution of the parameter space as a function of the dilution of CH_4 feedstock. While changing the pump and switching the MFCs have been able to increase the H_2 -to- CH_4 ratio and decrease the C_{CH_4} by about one order of magnitude (for a given CH_4 feedstock dilution), modifying the CH_4 feedstock concentration from 100 % down to 2000 ppm resulted in a 500-fold improvement (for a given gas flow

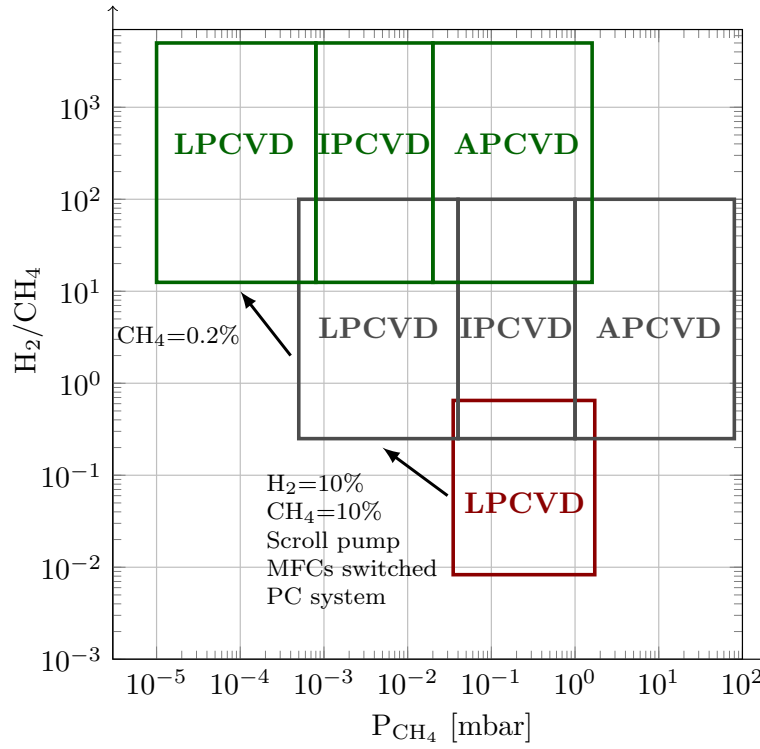


Figure 5.5: Log-Log plot representing the parameter space in terms of H_2/CH_4 and P_{CH_4} as a function of the various modifications that have been made to the CVD setup. The 3 zones in the grey and in the green squares represent the conditions that can be achieved using $P_{tot}=0.5$ mbar (LPCVD), $P_{tot}=1000$ mbar (APCVD) or intermediate pressure (IPCVD) regimes.

rate $F_{Ar/H_2}/F_{Ar/CH_4}$ ratio). As a consequence, adapting the gas feedstock dilutions represents an easier route to improve CVD conditions compared with switching the MFCs and replacing the pumping system. On the other hand, combining Eq. 5.2 and 5.3 leads to a direct relation between C_{CH_4} and the H_2 -to- CH_4 ratio:

$$C_{CH_4} = \frac{D_{CH_4} \times D_{H_2}}{D_{H_2} + R \times D_{CH_4}}. \quad (5.4)$$

This equation is plotted in Fig. 5.7 for $D_{H_2}=10\%$ and for different values of D_{CH_4} . This graph demonstrates that in theory, a high H_2 -to- CH_4 ratio and a low C_{CH_4} can be achieved with any CH_4 feedstock dilution. However, achieving for instance a value of $H_2/CH_4=1000$ in practice would require gas flow rate ratios ($F_{Ar/H_2}/F_{Ar/CH_4}$) of about 10000, 1000, 200 and 20 for CH_4 feedstock concentrations of 100%, 10%, 2% and 2000 ppm, respectively.

Using high $F_{Ar/H_2}/F_{Ar/CH_4}$ ratios does not represent a viable route for industrial production as it most likely results in an excessive consumption of the gas feedstocks. Moreover, using a high gas mainstream velocity promotes the Cu catalyst evaporation and negatively impacts graphene growth (thus justifying the use of Cu pockets or cuvettes as discussed in chapter 4).

Thanks to the various modifications that have been made to the initial LPCVD setup over the years, the current CVD setup now offers quite some advantages and new possibilities: (i) a wider range of CVD conditions (H_2/CH_4 , P_{CH_4} , C_{CH_4}) can be explored, (ii) the CVD protocol can be performed at low, ambient or intermediate pressure, (iii) the global pressure can be tuned as the CVD protocol proceeds which is essential to rigorously study the impact of CVD parameters on graphene growth (see chapters 6 and 7), (iv) the global pressure is more accurately monitored with the new gauges and the gas flow rates are more precisely controlled with the new mass flow controllers and, (v) the CVD system can be efficiently cleaned using the turbo pump mounted in parallel with the scroll pump. It is also worth noting that given the dilution levels of the gas feedstocks, the CVD furnace operates under industrially safe conditions.

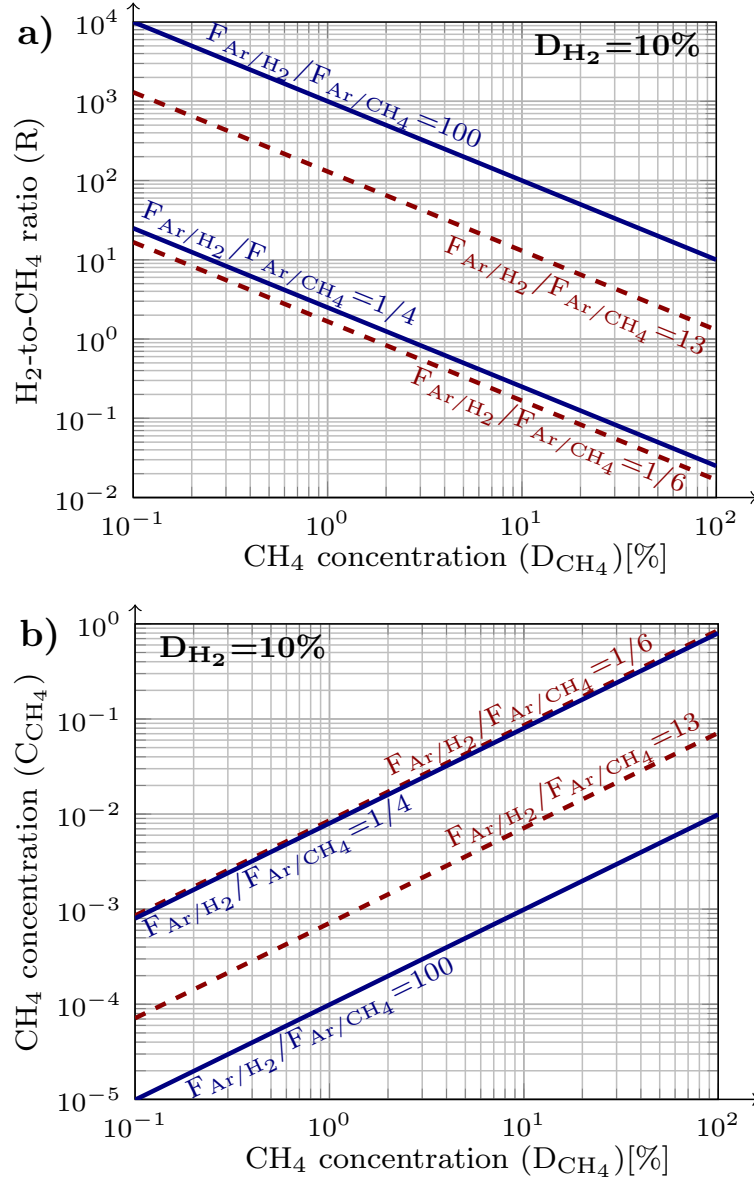


Figure 5.6: Log-Log plot representing the parameter space in terms of H_2/CH_4 and C_{CH_4} as a function of the CH_4 feedstock dilution. The surface areas delimited by the dashed red lines and by the solid blue lines represent the parameter spaces that could be achieved before and after switching the MFCs and replacing the pump, respectively. This representation is in accordance with tables 5.3 and 5.4.

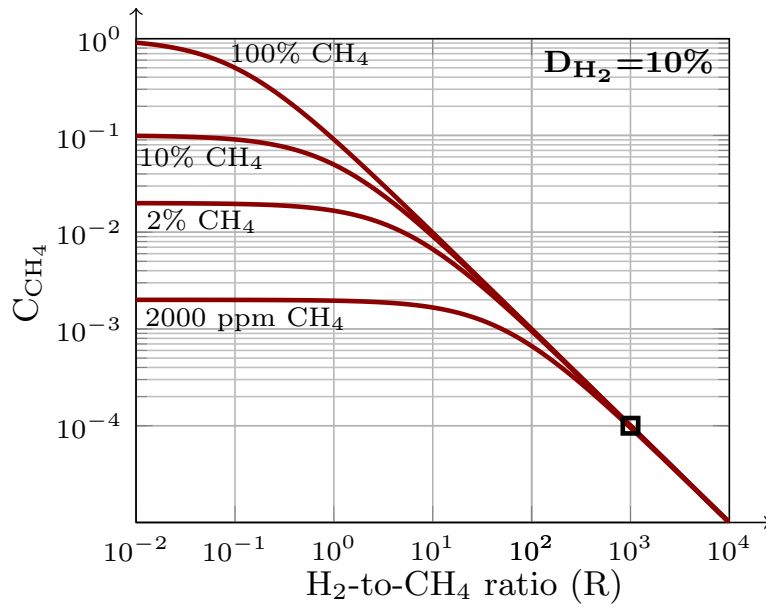


Figure 5.7: Log-Log plot representing the correlation between C_{CH_4} and H_2/CH_4 for different D_{CH_4} as obtained from the Eq. 5.4.

Chapter 6

Synthesis Results on Copper Films

This chapter presents the experimental method that has been conducted to determine optimal CVD conditions and synthesize millimeter-size graphene domains on top of thin Cu films. The successful growth of graphene domains with lateral dimensions exceeding the state-of-the-art has been mainly obtained by using appropriate gas compositions and precisely controlling the global pressure inside the CVD furnace during the successive steps of the graphene synthesis protocol: Cu substrate annealing, graphene nucleation and growth.

Section 6.1 motivates the utilization of thin Cu films instead of widely used Cu foils as catalyst for the graphene growth. Section 6.2 then describes why controlling the global pressure during the CVD synthesis protocol is essential to rigorously and systematically study the impact of CVD parameters on graphene growth. Section 6.3 presents the systematic study that has been conducted to determine optimal CVD conditions for the graphene growth step, that is, the conditions yielding large compact defect-free graphene domains (GDs). The focus is then shifted to the Cu annealing conditions with section 6.4 discussing the use of a reducing or an inert atmosphere and section 6.5 investigating which pressure level better contributes to the reduction of graphene nucleation sites. The next section investigates why increasing the pressure level of argon during the Cu annealing step decreases the nucleation site

density during the graphene growth step. For the sake of rigorousness and coherence, the CVD furnace has always been evacuated between the Cu annealing and the graphene growth steps. Section 6.6 shows that this extra step is crucial for maintaining the Cu film physical integrity upon the CVD process. Section 6.7 demonstrates that the Cu film thickness has very little or no influence on the graphene growth. Section 6.8 shows the outcome of the systematic study carried out in this chapter and provide some Raman characterization of the millimeter-size graphene domains. Finally, section 6.9 shows the best CVD results that have been produced and summarizes the main findings presented in this chapter.

6.1 Motivation

In contrast to widely spread Cu foils, using a thin Cu film deposited on a flat, smooth and rigid substrate offers exciting prospects for various reasons:

- 1. Graphene growth:** Cu films constitute an ideal alternative to Cu foils for rigorously studying the influence of CVD conditions on graphene growth because (i) given its fabrication process and its quasi two-dimensional nature, the Cu film features a higher purity and more particularly a lower carbon content which can yield an intrinsic lower nucleation site density and reduce the chance of producing few-layer graphene, (ii) its relatively smooth surface morphology circumvents the use of cumbersome pre-CVD treatments required to eliminate the surface morphology singularities which can act as preferential sites for graphene nucleation [89], (iii) heteroepitaxial Cu film can be used to control the orientation of graphene domains [135–137] and (iv) Cu films deposited on an inert substrate have only one single surface exposed to the CVD furnace atmosphere and prone to produce C species. As a result, graphene growth is exclusively dictated by surface reaction and does not depend on C species diffusion through the catalyst thickness [185].

- 2. Graphene transfer:** As graphene growth mimics Cu surface morphology, producing graphene on a smooth and flat Cu film results in a more planar graphene sheet and in turn, less wrinkles and cracks in the transferred graphene [186].
- 3. Processing:** Using a flat and rigid substrate improves graphene processability as it allows the direct processing of graphene on its synthesis substrate by conventional CMOS technologies [127].

Although a Cu film seems to be a more convenient platform for the realization of graphene-based practical applications and for the rigorous study of graphene growth mechanisms, the literature shows that Cu films are underexploited compared to Cu foils.

The key challenge for growing mm-size GDs on Cu film lies in maintaining the Cu film's physical integrity upon the high temperature CVD process while using appropriate CVD conditions. Cu film degradation arises mainly from Cu evaporation loss [139], Cu film dewetting [129] or Cu interdiffusion with the underlying substrate [132]. Using a shorter duration or a reduced temperature for the graphene growth step have been used to grow graphene while mitigating Cu degradation but these conditions are conflicting with the growth of compact large domains [133,134].

6.2 Pressure-Controlled Chemical Vapor Deposition

As presented in the tables in chapter 2, the vast majority of graphene growth studies published so far mostly focused on either the low pressure (LP) or ambient pressure (AP) CVD regime. It can also be observed in the same tables that both regimes yield large graphene domains with compact shapes, which presumes that the global pressure is not the determinant parameter for producing large high-quality domains. Nowadays, there does not seem to be a clear consensus within the scientific community that a specific pressure regime is more prom-

ising than the other in terms of graphene quality.

As explained in chapter 5, the LPCVD system that has been initially purchased has been customized so that the global pressure inside the quartz tube can be continuously adjusted from 0.5 to about 750 mbar. The upper pressure limit has been set to 750 mbar in order to reduce the risk of reaching an overpressure that would pull the flanges out of the quartz tube extremities and break the hermetic sealing.

In order to shed some light on the role of the global pressure in the formation of graphene and rigorously determine which pressure level is the most appropriate to produce large high-quality graphene domains, it is of central importance to achieve optimal methane partial pressure conditions for every investigated global pressure level. Maintaining a partial pressure of methane as close as possible from the nucleation threshold is essential for producing a low density of domains that will be able to expand over hundreds of microns before merging with others. Using a methane partial pressure (P_{CH_4}) far beyond the threshold would result in excessive adsorption of methane molecules on the Cu surface, in a higher supersaturation of active C species and, in turn, in the formation of a high density of nucleation sites [53].

Unfortunately, predicting the methane partial pressure corresponding to the nucleation threshold is challenging since it strongly depends on many factors including the catalytic substrate preparation and the desorption rate of active C species from the Cu surface (which is mainly dictated by the CVD furnace temperature and global pressure). Therefore, determining an approximate value of the lowest P_{CH_4} that allows the nucleation of graphene requires to conduct several experiments with a precise control of the methane partial pressure. The precise monitoring of P_{CH_4} is achieved by tuning the flow rates of Ar/H₂ (F_{Ar/H_2}) and Ar/CH₄ (F_{Ar/CH_4}) injected into the CVD furnace and is calculated according to

$$P_{\text{CH}_4} = P_{\text{tot}} \times \frac{F_{\text{Ar/CH}_4} \times D_{\text{CH}_4}}{F_{\text{Ar/CH}_4} + F_{\text{Ar/H}_2}}, \quad (6.1)$$

where D_{CH_4} is the dilution of the Ar/CH₄ (2500 ppm) gas flow feedstock. For a given global pressure (P_{tot}), using a higher Ar/H₂ gas flow results in a higher dilution of the methane in the gas phase (i.e. a lower methane partial pressure) and a higher hydrogen-to-methane ratio (R) which is calculated by:

$$R = \frac{F_{\text{Ar/H}_2} \times D_{\text{H}_2}}{F_{\text{Ar/CH}_4} \times D_{\text{CH}_4}}, \quad (6.2)$$

where D_{H_2} is the dilution of the Ar/H₂ (10%) gas mixture feedstock. Although these equations are rather accurate for the LPCVD regime, they are not valid for the APCVD regime as they assume that the CVD furnace is free from any gas prior to the injection of CH₄ and H₂. Carrying out the CVD protocol at ambient pressure implies that the CVD furnace is pre-filled with the gas phase employed for the Cu annealing step prior to the injection of methane and hydrogen. Precisely monitoring the gas composition for the APCVD regime would require the use of expensive gas sensors or the use of more complex time-dependent equations as H₂ and CH₄ would mix with the pre-existing phase.

In this regard, the pressure control system is an efficient tool to address these limitations. When dealing with pressure levels exceeding 1 mbar during the Cu annealing step, the valve can be opened to purge the gas contained in the CVD furnace prior to injecting methane and hydrogen for the graphene formation. Regardless the gas composition or global pressure level present in the CVD furnace, purging the furnace at the end of the Cu annealing step "resets the gas history" of the furnace and ensures the precise control of CVD conditions during the graphene growth step.

6.3 Graphene growth conditions

The first step towards the synthesis of millimeter-size compact single-layer graphene domains consists of determining the CVD processing parameters (T_{Gr} , P_{Tot} , F_{Ar/CH_4} and F_{Ar/H_2}) and more particularly the graphene growth conditions (T_{Gr} , P_{tot} , P_{CH_4} and R) favoring a low density of nucleation sites as well as a non-dendritic growth front. The temperature, gas flows and global pressure profiles used for this study are illustrated in Fig. 6.1.

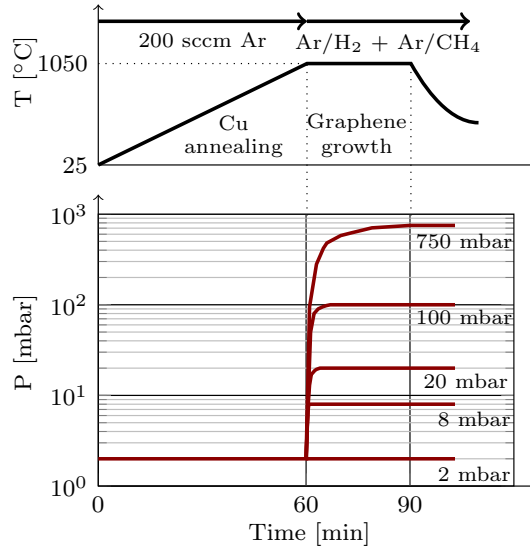


Figure 6.1: *Temperature, gas flow and global pressure profiles used for studying the impact of CVD conditions on graphene growth.*

To provide a rigorous analysis, the Cu film annealing step is performed under identical conditions, regardless of the pressure used for graphene growth step. Using low pressure conditions (2 mbar) prior to the introduction of methane and hydrogen ensures that the gas phase composition inside the CVD furnace during the growth stage is exclusively dictated by the gas injected since the beginning of the growth stage. Once the

graphene growth temperature ($T_{gr}=1050\text{ }^{\circ}\text{C}$) is reached, Ar/H_2 and Ar/CH_4 gas flows are introduced in the CVD furnace and the aperture of the metering valve located downstream of the CVD furnace is adjusted. The pressure increases and stabilizes at a value determined by the metering valve aperture and the total gas flow introduced.

Figure 6.2 summarizes the outcome of the graphene growth experiments conducted in this work. Although no graphene formation has been observed for graphene growth performed at 2 mbar, graphene has been synthesized under various H_2 -to- CH_4 ratios for all the pressure levels investigated here including 8, 20, 100 and 750 mbar.

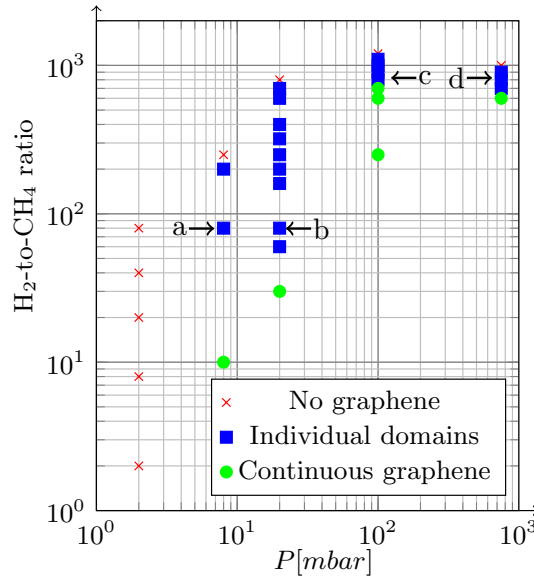


Figure 6.2: Log-log plot summarizing the graphene growth outcome as a function of P_{tot} and the H_2 -to- CH_4 ratio conditions used for the different CVD experiments described in Fig. 6.1.

Low methane dilution levels result in continuous graphene sheets (green circles) while excessive methane dilution levels do not yield any graphene formation (red crosses). Intermediate dilution levels (blue squares) cor-

respond to the growth of graphene nuclei which are sufficiently separated from each other that individual GDs can be observed by the means of the SEM. The obtained graphene domain density and size plots corresponding to these experiments are displayed in Fig. 6.3.

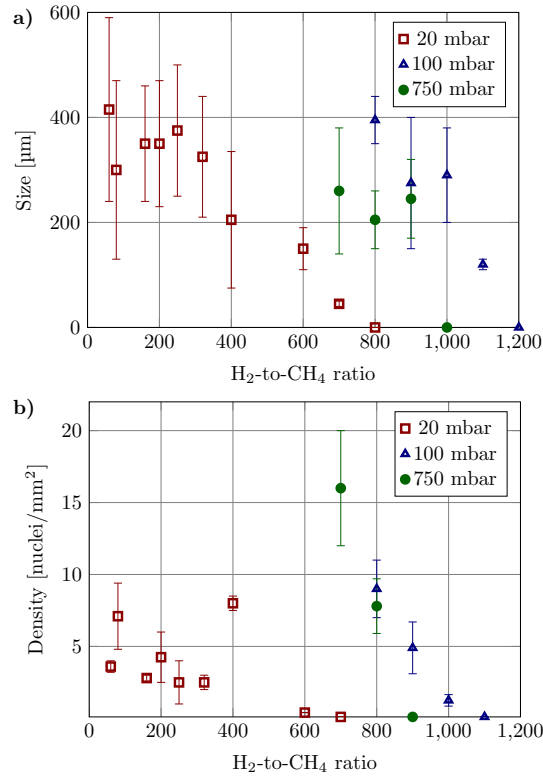


Figure 6.3: Plots summarizing the graphene domain (a) size and (b) density as a function of H_2 -to- CH_4 ratio for different global pressure regimes. The data points only represent the CVD experiments that resulted in the growth of individual graphene domains as shown in Fig. 6.2.

Figure 6.3a shows that increasing the H_2 -to- CH_4 ratio (and thus increasing the dilution of methane in the gas phase) leads to a reduction of the graphene domain size. This observation is a clear evidence of

the etching effect of hydrogen on graphene as described in chapter 2. Figure 6.3b shows that at higher global pressure (or higher hydrogen-to-methane ratio), a higher partial pressure of methane is required to trigger graphene nucleation. Although a higher pressure is supposed to facilitate the formation of stable nuclei (through the reduction of Cu sublimation), the presence of a higher quantity of hydrogen in the gas phase prevents the formation of graphene nuclei that are stable enough to expand and form large-area graphene crystals eventually. As a low nucleation site density (≤ 0.05 nuclei/mm²) can be obtained for all pressure levels investigated here including 8, 20, 100 and 750 mbar, it seems that the global pressure is not a decisive parameter for the lateral size of produced GDs.

More interestingly, Fig. 6.2 shows that graphene formation can be achieved under higher H₂-to-CH₄ ratios when the CVD process is performed under higher global pressure. The maximum H₂-to-CH₄ ratio that can be used to produce graphene shifts from about 200 to about 700 when the global pressure is raised from 8 to 20 mbar and can even reach about 1100 when the global pressure equals 100 mbar. Increasing the pressure and the H₂-to-CH₄ ratio clearly affects the growth of graphene domains as shown in Fig. 6.4. Even though graphene domains grow in a form tending to hexagon-like shapes indicating a coherent atomic structure (6.4, left panel), the growth front differs a lot (6.4, right panel). Producing graphene at a relatively low pressure results in a highly dendritic growth front and partially hollow graphene domains (see Fig. 6.4a). Increasing the global pressure and the H₂-to-CH₄ ratio yields denser graphene domains (i.e. featuring thinner graphene-free veins) as well as smooth edges. Although the dendritic aspect can be reduced by increasing the H₂-to-CH₄ ratio while maintaining the same global pressure, this ratio has to remain relatively low to avoid excessive dilution of methane and allow graphene formation. Furthermore, our experiments show that even if the H₂-to-CH₄ ratio is exactly the same (R=800 in Figs. 6.4e and 6.4f), an increase of global pressure produces smooth edges instead of jagged edges. As a consequence, we believe that using higher pressure conditions is a key CVD parameter for the growth of high-quality graphene.

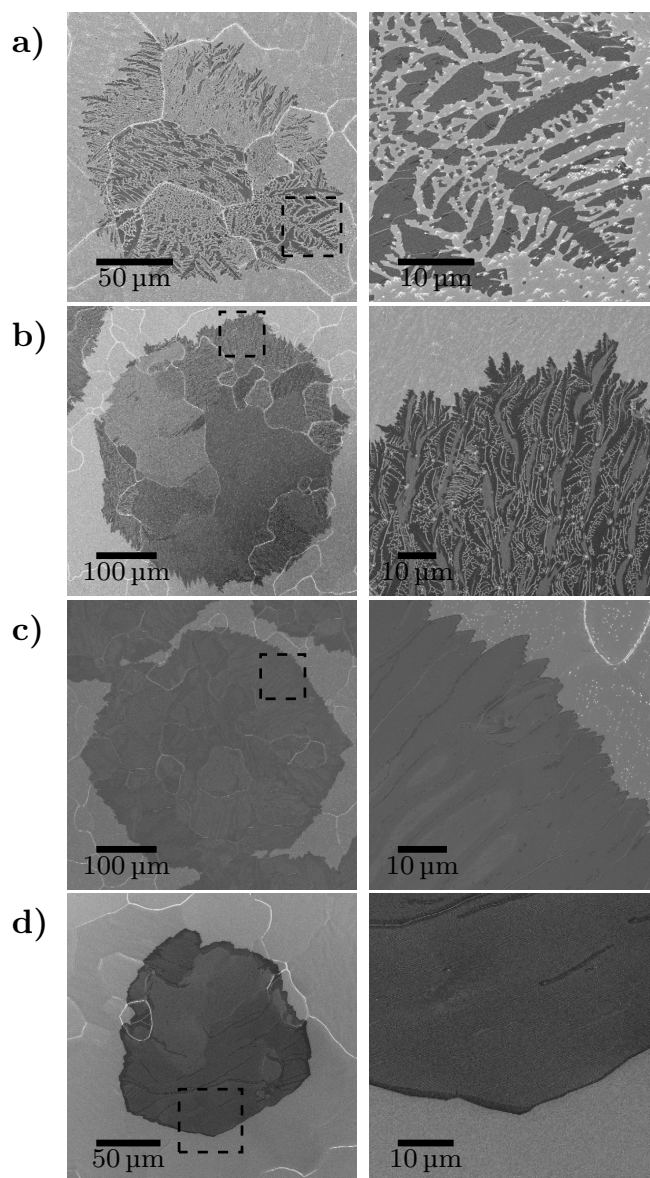


Figure 6.4: *In-lens SEM images of graphene grown on Cu under a pressure of (a) 8 mbar, (b) 20 mbar, (c) 100 mbar and (d) 750 mbar. Right panel images are higher magnification images of the left panel framed square areas. The different domains have been grown using the CVD conditions pointed out with arrows in Fig. 6.2.*

The significant modification of graphene crystal morphology with the global pressure and H_2 -to- CH_4 ratio can be explained by considering the interplay of complex processes including the diffusion of active C species adsorbed on the Cu surface, the attachment of these C species on the growing GD and the competition between the growth and etching of graphene induced by the presence of hydrogen in the gas phase [82,88]. The highly dendritic front obtained at lower pressure most likely arises from the combination of a relatively low concentration of active C species adsorbed on the Cu surface and a relatively high growth rate of the branches of GDs. The low pressure conditions favor a low concentration of C species due to a low adsorption rate of methane (resulting from a low partial pressure in the gas phase) and a high desorption rate of C species (induced by Cu sublimation). On the other hand, the etching effect of hydrogen has a limited impact due to the low amount of hydrogen present in the gas phase. As a result, graphene protrusions in the growth front propagate radially and deplete their surrounding in C species. This depletion hinders the lateral growth of dendritic graphene branches and the formation of dense GDs. On the contrary, the smooth edges and dense graphene domains achieved under relatively high pressure conditions and high H_2 -to- CH_4 ratios are most likely the result of a relatively high concentration of C species on the Cu surface available for the formation of graphene and a strong competition between graphene growth and graphene etching at the growth front.

6.4 Cu annealing atmosphere composition

Another major milestone toward the synthesis of large-area GDs consists of decreasing the nucleation site density by employing appropriate conditions during the warming ramp of the CVD furnace. Although most of the CVD process reported in the literature employed a reducing atmosphere in the CVD furnace prior to the graphene growth step [51,78,127,187], a few recent reports demonstrated that using an inert atmosphere could be beneficial for the growth of graphene [85,87,104,113]. A first crucial step towards the determination of optimal conditions for the Cu annealing step consists of comparing the growth of graphene after performing the Cu annealing/warming ramp step under either a reducing atmosphere (made of an Ar/H₂ (10%) gas mixture) or an inert atmosphere (made of pure Ar).

The annealing step is performed under a low global pressure (2 mbar) of either pure Ar (Fig. 6.5a) or Ar/H₂ mixture (Fig. 6.5b) in order to facilitate the precise control of the gas composition inside the CVD reactor during the graphene growth step. Indeed, using a low pressure during the annealing step ensures that the gas phase composition during the graphene growth step is independent on the gas composition used during the annealing step and hence circumvents the use of a gas evacuation step prior to graphene growth.

Figure 6.5b exhibits two different pressure and temperature profiles. The CVD experiment described by the dark red dashed profile has been first performed as it corresponds to the reference experiment shown Fig. 6.5a. The 30 min-long graphene growth step yields a continuous graphene layer (in contrast to the growth of individual graphene domains obtained with an Ar annealing as shown in Fig. 6.5c). As a continuous graphene sheet does not permit the observation of the domain density and lateral size, different CVD experiments with the exact graphene growth conditions but shorter durations have been experimented. It appears that the graphene growth step has to be interrupted after 5 min to prevent the coalescence of individual graphene domains (see Fig. 6.5d). After a 5 min graphene growth step, the global pressure into the CVD fur-

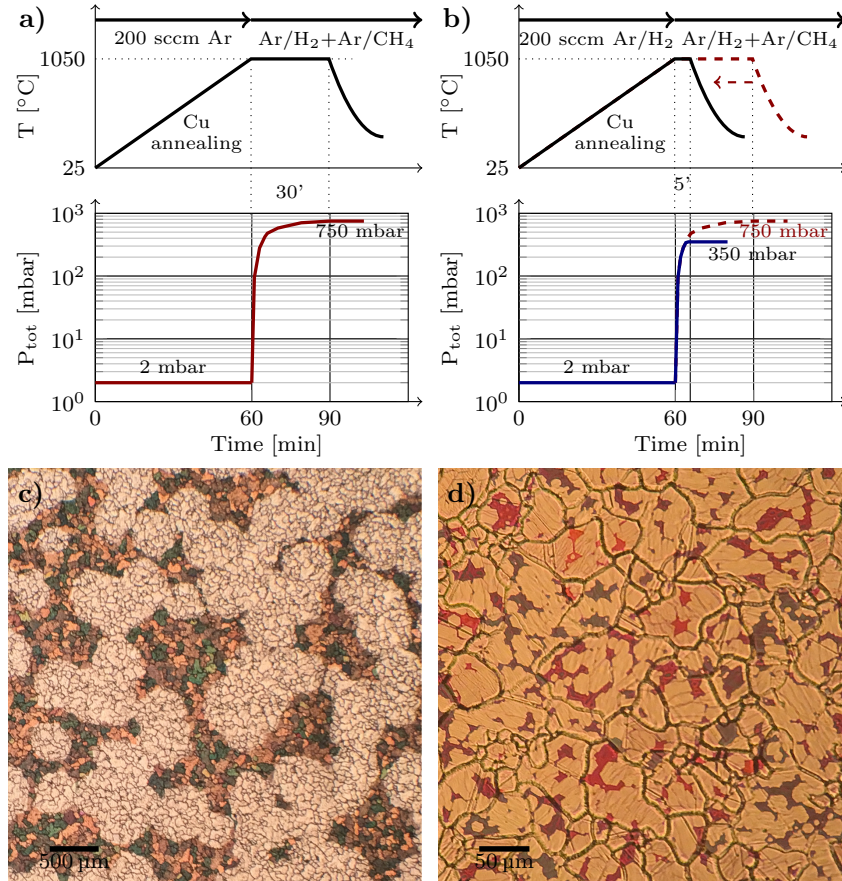


Figure 6.5: *a-b) Temperature, global pressure and gas flow profiles of the CVD experiments performed to emphasize the impact of the Cu annealing atmosphere composition on the growth of graphene. a) Experiment employing pure Ar during the annealing step (reference experiment). b) Experiment using a reducing atmosphere (Ar/H₂ (10%)) during the annealing step. Optical microscope images in (c) and (d) show the Cu surface (after a slight post growth Cu oxidation step used to make graphene visible) resulting from the CVD experiments presented in (a) and (b), respectively.*

nance reaches only 350 mbar as shown in Fig. 6.5b. Performing such a short duration graphene growth would not lead to any graphene formation if the Cu annealing step was performed under an argon atmosphere.

Even though using a low annealing pressure results in a limited reducing/oxidizing effect, the nucleation site density and the domain size differ a lot. Using an argon atmosphere results in the formation of graphene domains with a lateral size of ~ 300 microns and a nucleation site density of about 400 nuclei/cm^2 . In contrast, annealing the Cu substrate in hydrogen produces graphene domains with a lateral size inferior to ~ 30 microns and a domain density of about $3 \times 10^5 \text{ nuclei/cm}^2$.

The early formation of graphene on the Cu substrate annealed in Ar/H₂ (less than 5 minutes) compared with the Cu substrates annealed in pure Ar (about 12 min) and the substantially higher domain density (by about 3 orders of magnitude) suggest that a high concentration of active C species are already present on the Cu surface at the onset of the graphene growth step. This high concentration of C species may stem from the transport and the catalysis of gaseous organic compounds on the Cu surface during the annealing step. The high concentration of hydrogen and the absence of methane prevents the formation of stable nuclei prior to the graphene growth step but does not hinder the accumulation of C species on the catalytic surface. These gaseous compounds are believed to come from the etching of graphene (pre-deposited in the CVD furnace upon previous CVD runs via the sublimation and re-deposition of Cu) induced by hydrogen or by the pyrolysis of organic compounds introduced in the CVD furnace during the handling and processing of the synthesis substrate.

6.5 Cu annealing pressure conditions

Another crucial step towards the determination of optimal conditions for the Cu annealing step consists of studying which pressure level provides the best results in terms of graphene domain density and structural density. This section demonstrates that the Ar pressure level present in the CVD furnace during the warming ramp of the CVD protocol significantly affects graphene nucleation density. To illustrate this statement, another series of graphene growth experiments has been conducted using identical graphene growth step but different annealing pressure conditions. In order to apply the exact same graphene growth conditions (temperature, global pressure and gas composition profiles) in each experiment regardless the Ar pressure used during the annealing, the CVD furnace is evacuated for 5 minutes prior to the introduction of hydrogen and methane as shown in Fig. 6.6a.

Figure 6.6b represents the evolution of nucleation site density with the Ar pressure used during the Cu annealing step. The nucleation site density values have been estimated by manually counting the graphene domains made visible by a post-CVD slight oxidation of the Cu surface. The counting has been carried out by observing 4 areas of $\sim 1.2 \text{ cm}^2$ randomly chosen on the 3-inch catalytic wafer ($\sim 44 \text{ cm}^2$) used for the experiment. Due to rather small variation in local graphene nucleation site density, the 4 estimated dots might overlap and not be visible for each annealing global pressure level. Our observations clearly show a drastic drop of the nucleation site number by nearly 3 orders of magnitude when Ar pressure is increased from 2 up to 750 mbar. Optical microscopy images corresponding to Ar annealings performed at 20, 50, 200 and 500 mbar are showed in Fig. 6.6c, Fig. 6.6d, Fig. 6.6e and Fig. 6.6f, respectively.

It can also be observed by comparing Fig. 6.6c to Figs. 6.6d-f that using a higher Ar pressure upon the Cu annealing decreases the apparent graphene growth rate. This tendency is particularly noticeable for relatively low Ar pressure, that is in the 2-50 mbar range.

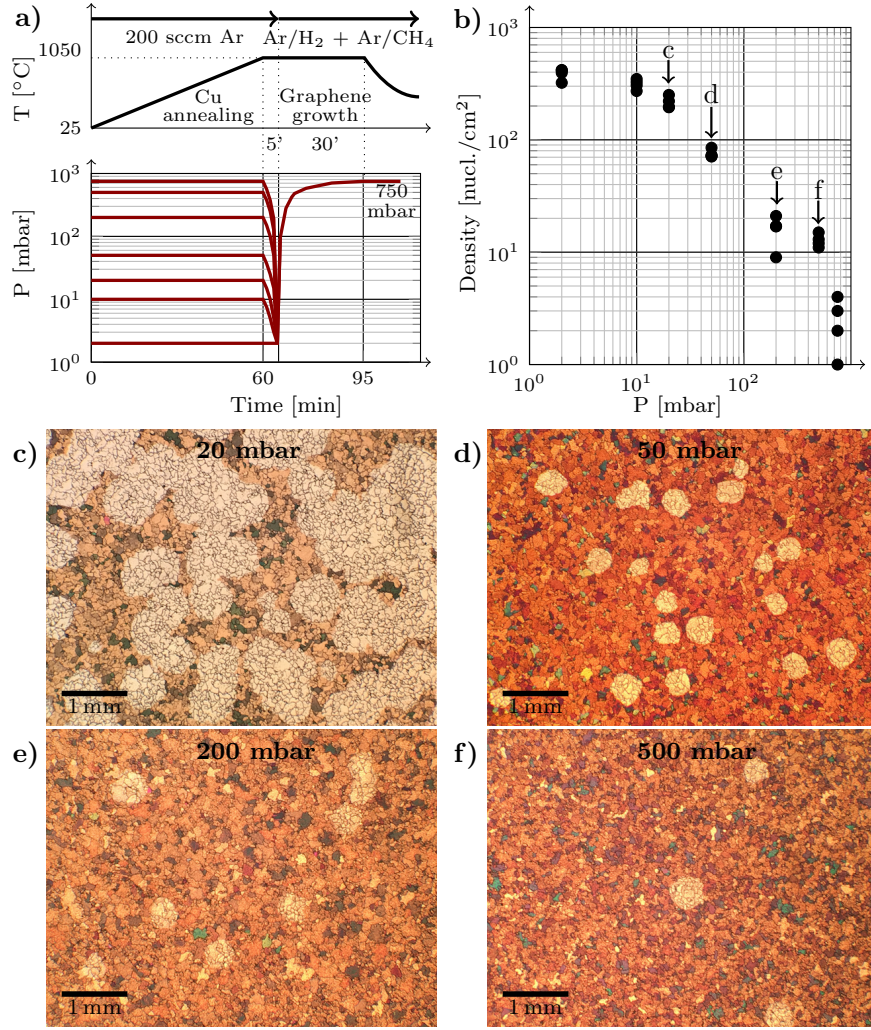


Figure 6.6: a) Temperature, gas flow and global pressure profiles used for the various CVD experiments. b) Log-log plot showing the evolution of the graphene domain density with the Ar pressure level used during the Cu annealing/ramping step. (c-f) Optical microscope images of samples annealed under 20 mbar (c), 50 mbar (d), 200 mbar (e) and 500 mbar (f) of Ar, respectively.

Additional experiments have been carried out in order to shed some light on how the Ar pressure level influences the growth of graphene. These experiments mainly focused on observing the evolution of the Cu substrate upon the annealing step, prior to any graphene formation. For this purpose, the 2 extreme cases presented in Fig. 6.6a, that is, the CVD protocols involving an annealing step under 2 mbar and under 750 mbar of argon, have been further examined.

To get an insight about how the Cu surface looks like directly after the annealing step and prior to the graphene growth step, the Cu surface has been observed after carrying out the two experiments illustrated in Fig. 6.7a. As shown in Fig. 6.7c and Fig. 6.7d, heating up the Cu substrates in an Ar atmosphere creates a colorful compound on the Cu surface. The nature of this compound turns out to be Cu oxide, as identified using energy dispersive X-ray (EDX) and scanning electron microscopy (SEM). The amount of Cu oxide produced during the annealing step seems to depend on the argon pressure as low pressure conditions (2 mbar) yields only a few Cu oxide islands while high pressure conditions (750 mbar) results in the formation of an almost continuous Cu oxide layer. Although the argon supply used here is supposed to be inert and pure (Ar 6.0 Research Grade, 99,9999% pure, Praxair), it appears to have a slight oxidizing effect. This effect, probably due to the presence of oxidizing impurities ($\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 0.2$ ppm), increases with global pressure.

Recently, a few research groups demonstrated that mildly oxidizing the Cu catalytic surface effectively contributes to decreasing the nucleation site density [85, 87, 102–104, 113, 188]. However, these works differ on explaining how oxygen actually impacts the synthesis substrate and graphene growth. The reduction of nucleation site density has been ascribed to (i) a modification of Cu surface morphology [87, 113], (ii) the presence of a catalytic inactive oxide layer at the beginning of graphene growth [85], (iii) the passivation of Cu active sites [102, 104], (iv) the removal of surface impurities [87, 188] and, (v) the reduction of the carbon content in the Cu catalyst [103, 188].

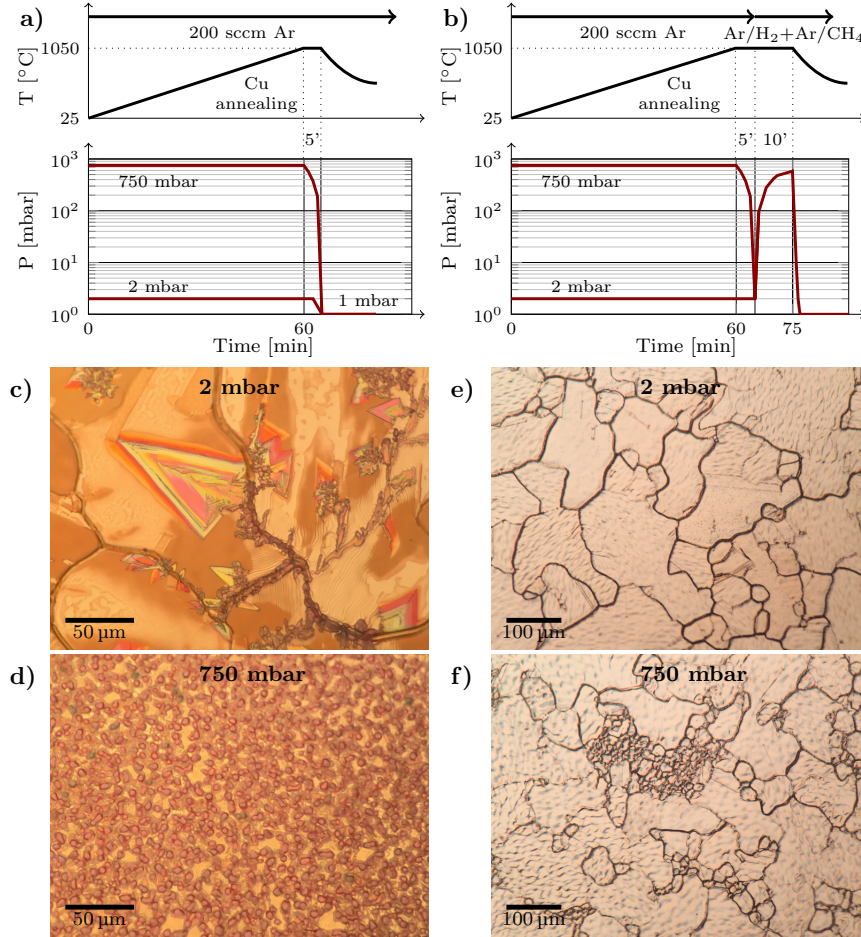


Figure 6.7: *a-b) Temperature gas flow and global pressure profiles of 2 sets of experiments used to (a) determine how Ar atmosphere affects the Cu surface during the warming ramp and (b) gain more insight on how the Cu surface evolves at the onset of graphene growth. c-f) Optical microscope images of the Cu surface after the experiment described in (a) under an Ar pressure of (c) 2 mbar and (d) 750 mbar and described in (b) under an Ar pressure of (e) 2 mbar and (f) 750 mbar.*

To better understand how the use of an oxidizing atmosphere during the annealing step plays a role in drastically reducing the nucleation sites during the subsequent graphene growth step, we focused on gaining more insight about how the catalytic substrate evolves in the very early stage of the graphene growth step, that is when Ar/H₂ and Ar/CH₄ flows are injected inside the CVD furnace.

In this regard, The exact same experiments as in Fig. 6.6 have been performed but the graphene growth step has been interrupted after a 10 min exposure to the reducing atmosphere composed of H₂, CH₄ and Ar (see Fig. 6.7b). This short duration growth step does not trigger any graphene growth, most likely because the Cu surface is not exposed for a sufficient time to the carbon source to start the nucleation. To ensure no extra oxidation/reduction during the cooling step in the CVD protocols displayed in Figs. 6.7a and 6.7b, the furnace is rapidly evacuated down to a pressure of 1 mbar. As a consequence, observing the Cu substrate after these experimental tests provides an insight into the Cu surface condition shortly before the onset of graphene formation. It appears that the Cu oxide induced during the annealing step completely vanished, probably turned into metallic Cu due to the reducing atmosphere. Additional experiments also showed that the continuous oxide layer obtained by annealing the Cu under 750 mbar of argon was getting completely reduced upon the 2 first minutes of exposure to the reducing atmosphere (results not shown). These observations suggest that the Cu oxide layer does not directly interact with the growth of graphene and cannot act as a reversible passivation layer which gradually vanishes as graphene growth proceeds as any traces of Cu oxide is reduced way before graphene formation starts.

Although the Cu surface morphology and oxidation level differ a lot depending on whether it has been annealed under 2 or under 750 mbar of argon, it is relatively similar once the Cu substrates have been exposed to the Ar/H₂/CH₄ gas mixture for 10 min (Fig. 6.7e-f). The formation of more Cu oxide during the warming ramp hinders the Cu grain microstructure evolution upon annealing and leads to puddles of

smaller Cu grains (Fig. 6.7f). However, no correlation has been found between these puddles and the location of graphene nuclei. Moreover, no Cu surface singularities/protrusions have been observed in the center of the graphene domains as observed on Cu foils by Luo *et al.* [113]. Therefore, we do not believe that a surface morphology modification is the key factor for reducing the nucleation site density by almost 3 orders of magnitude.

We believe that the nucleation site density is strongly affected by the accumulation of active C-based species on the Cu surface during the annealing step. These C-based species may originate from various sources including (i) the pyrolysis of organic compounds introduced in the CVD furnace during the loading of the synthesis substrate, (ii) previous CVD processes which brought C-based compounds inside the furnace (through methane cracking, particularly promoted by evaporation/re-deposition of Cu on the inner walls [75]) or even (iii) directly from the bulk of the Cu catalyst as proposed by Kraus *et al.* [103] which is the less likely reason here given the thickness and the fabrication process of the Cu film. During the annealing, organic compounds vaporize in the gas phase and preferentially react on the catalyst. When annealed in an Ar atmosphere, the Cu surface gradually oxidizes (through the presence of oxidizing agents present in the Ar feedstock) and forms a reversible passivation layer which reduces the accumulation of C-based species on the surface. Moreover, the oxidizing agents contribute to neutralizing organic compounds (through formation of CO and CO₂) present in the furnace [188].

We believe that both the oxidative removal of C atoms in the CVD furnace and the C-species impoverishment on the Cu surface induced by the Cu oxide passivation layer effectively contribute to lowering the nucleation site density. This effect is even more significant as the Ar pressure (i.e. the oxidizing effect) is important. The high nucleation site density obtained following a Cu annealing in a reducing atmosphere can be explained by the formation of highly volatile hydrocarbons (C_xH_y) produced by H₂-induced etching of existing graphene in the furnace or newly created by reduction of freshly introduced parasitic organic compounds.

Moreover, maintaining a reduced Cu catalytic surface makes it more reactive for catalyzing the undesired C-based compounds transported by the gas phase.

The manifestation of a more effective C species depletion on the Cu surface with higher Ar pressure during the annealing can also be observed in Figs. 6.6c-f. Given that the growth conditions are exactly the same in the different CVD experiments, it is unlikely that the different domain sizes arise from different graphene growth rates. The smaller domain size achieved on the Cu substrate annealed under an Ar pressure equal or greater than 50 mbar is most likely induced by a graphene nucleation delay compared with the Cu substrate annealed under lower Ar pressure. Intuitively, a Cu substrate which is depleted in C species at the onset of the graphene growth step will require a longer duration to catalyze methane and achieve a sufficient concentration of C-based species to trigger graphene nucleation.

6.6 Hydrogen embrittlement

From the above observations, it might be tempting to perform both the Cu annealing and the graphene growth at high pressure, without proceeding to the evacuation of the chamber prior to the graphene growth step (shown in Figs. 6.6 and 6.7). However, it has been observed that directly introducing methane and hydrogen in the CVD furnace containing a high pressure of Ar results in the Cu film solid-state dewetting as shown in Fig. 6.8.

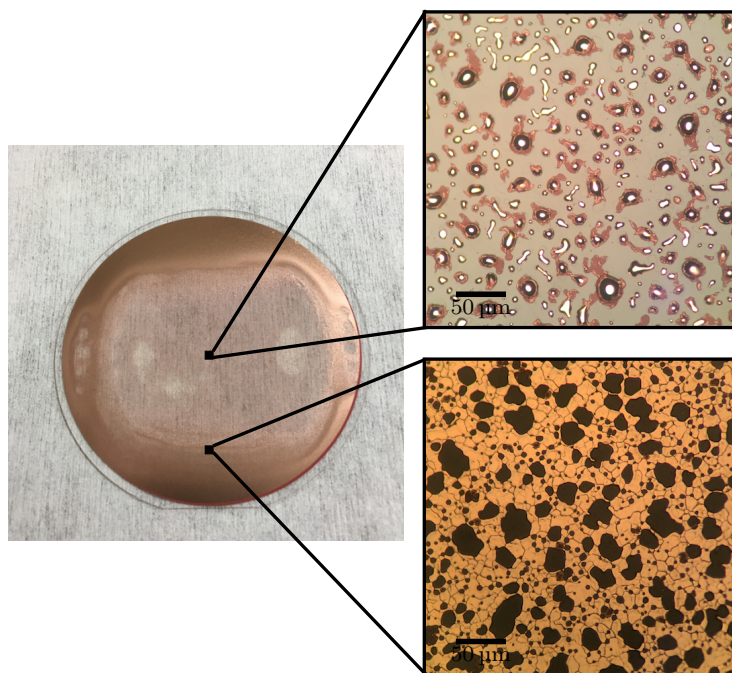


Figure 6.8: Photograph of the film deposited on a 3-inch fused quartz wafer after performing a CVD process involving a relatively high Ar pressure (500 mbar) during the Cu annealing step and no furnace evacuation prior to the graphene growth step. Optical microscope images show the extent of the dewetting phenomenon in two different locations on the substrate.

The dewetting of thin Cu films upon the CVD process has already been observed and attributed to excessive Cu evaporation induced by high temperature and low pressure conditions used for graphene growth [129].

Here, however, we intentionally used Cu films with a thickness of at least 1 micron and limited the high temperature step duration to maximum 90 min to deal with the sublimation-induced Cu film dewetting issues. Moreover, it is unlikely that the excessive Cu sublimation is responsible for the dewetting observed here as it occurs at the onset of the graphene growth step. It is found that the extent of dewetting strongly depends on the Ar pressure level used during the Cu annealing step. While no dewetting is observed for Ar pressure levels under 10 mbar, the Cu film degradation gets more pronounced as the Ar pressure is increased. This observation is rather intriguing given that using high pressure levels during the Cu annealing supposedly helps maintaining the Cu vapor close to the Cu surface and thus contributes to suppress the Cu evaporation loss.

It is believed that the Cu dewetting results from the reaction between hydrogen absorbed from the atmosphere and oxygen present inside the copper film which forms water vapor that decreases the cohesion between Cu grains. This phenomenon, called hydrogen embrittlement, is known to make bulk metals porous upon hydrogen annealing [189,190]. It seems that the presence of the thin Cu oxide layer on the Cu top surface does not play a role as evacuating the chamber does not remove that oxide layer. However, evacuating the furnace for 5 min might either reduce the oxygen content in the Cu film or slow down the arrival of hydrogen on the Cu surface and thus prevent any formation of water vapor in the Cu matrix. As a consequence, the evacuation of the CVD chamber prior to graphene growth is always performed to obtain mm-size GDs.

6.7 Impact of Cu thickness on graphene growth

In order to determine the impact of the Cu film thickness on the graphene growth, graphene has been produced on four different Cu films with varying thicknesses (800, 1600, 2400 and 4400 nm). The minimum thickness is chosen to be 800 nm in order to be able to perform a 50 min graphene growth step and to use an intermediate Ar pressure level (50 mbar) during the Cu annealing step without inducing solid-state dewetting. Using longer duration graphene growth step and/or higher Ar pressure levels during the annealing step would make the Cu film more prone to degradation (voiding and dewetting) which disrupts the proper growth of graphene. The maximum film thickness investigated here (4400 nm) is limited by the amount of metal that can fit into the crucible in the e-beam evaporation equipment. In order to apply the exact same CVD conditions to the Cu films with different thicknesses, the four substrates have been loaded in the CVD furnace together. The graphene domain density and size distribution have been evaluated by observing four different surface areas of $\sim 1.2 \text{ cm}^2$ randomly chosen on each Cu substrate.

Figures 6.9a and 6.9b show that the density and the lateral dimension of graphene domains do not seem to be affected by the Cu film thickness. This observation is consistent with the fact that the solubility of carbon in Cu is extremely low and the CVD growth of graphene on Cu catalyst is a surface mediated process [78]. Although there is a strong correlation between the Cu film thickness and the Cu grain size as shown in Fig. 6.10, it seems that the Cu grain boundaries have very little or no influence on the growth of graphene. Obtaining similar graphene growth results on Cu films with varying thicknesses supports the fact that the active C species responsible for the nucleation of graphene at the onset of graphene growth most likely comes from the gas phase and not from the residual carbon content of the Cu catalyst.

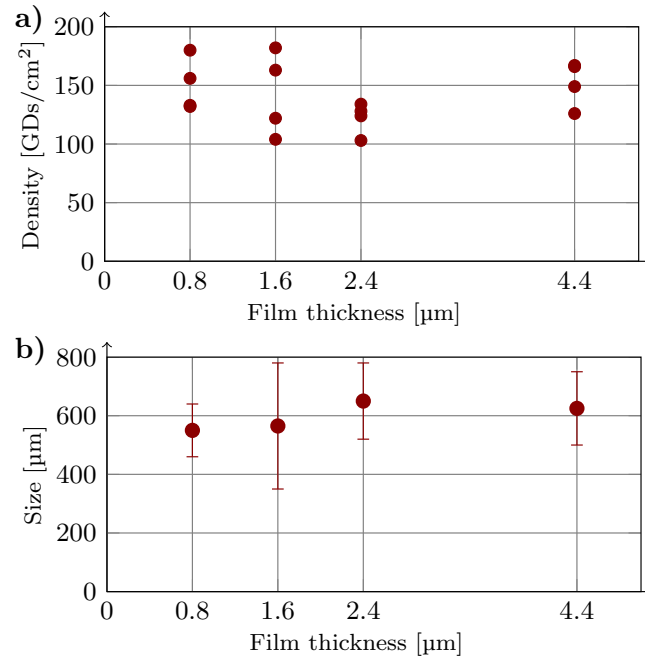


Figure 6.9: Influence of the Cu film thickness on the growth of graphene: (a) density and (b) lateral size of graphene domains as a function of the Cu film thickness. For each Cu film substrate, four different locations have been analyzed and plotted as data point in the plots.

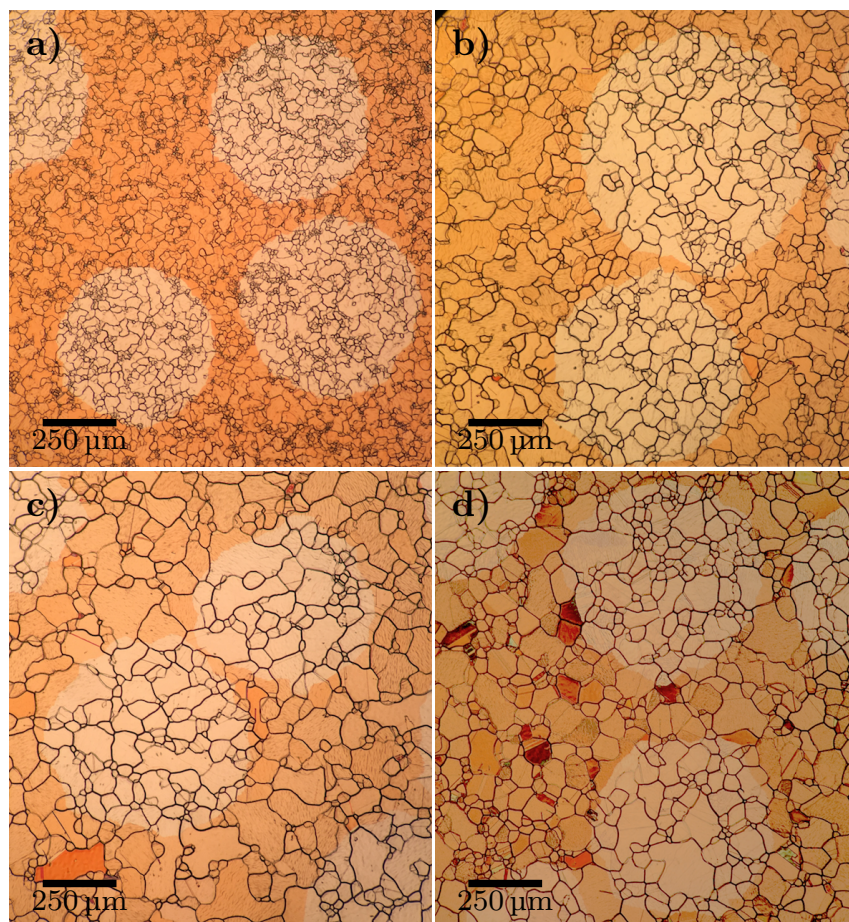


Figure 6.10: Influence of the Cu film thickness on the growth of graphene: Optical microscope images of the Cu surface after a slight post-CVD oxidation to make graphene visible. Images (a), (b), (c) and (d) correspond to Cu films with a thickness of 800, 1600, 2400 and 4400 nm, respectively.

6.8 Characterization of millimeter-size domains

Photograph (Fig 6.11a), optical microscopy image (Fig. 6.11b) and scanning electron microscopy (SEM) images (Fig. 6.11c-d) show mm-size graphene domains as produced on a 1200 nm-thick Cu film deposited on a 3-inch quartz wafer. Graphene is made visible directly after the CVD process by heating the substrate on a hot plate at 150°C for 5 min in air as shown in Figs. 6.11a and 6.11b [172].

A 30 min growth step results in GDs of a few hundreds of microns that can be easily distinguished from each other with bare eyes as shown in Figs. 6.11a. Extended graphene growth durations result in graphene domains with lateral size exceeding 1 millimeter after about 1 hour (see Fig. 6.11b) and the completion of a continuous graphene sheet after about 90 min. Graphene domains exhibit a rather compact shape consisting of a mixture of rounded and straight edges forming ~ 120 degree corners similarly to hexagons.

The hexagon-like shape of GDs, indicating a coherent atomic structure within the entire domain, suggests that these domains are single-crystalline. The non strictly straight growth front and hexagonal shape of graphene domains grown on Cu films most likely result from the fact that these GDs span over several adjacent Cu grains when they reach a lateral size of about 1 mm. These different Cu grains can be responsible for slight local variations in growth condition as different Cu surface crystallographic orientations present different catalytic activities, diffusion rates for adsorbed species and carbon precursor adsorption/desorption rates [191–193].

Except the bilayer regions with lateral size of a few microns occasionally found near the graphene domain edges (see dashed circle in Fig. 6.11f), the clear uniform color contrast shown in the SEM images (Figs. 6.11c,d) and optical microscopy images of graphene transferred on a 90 nm-thick SiO₂/Si substrate reflects the single layer nature of the produced graphene sheet.

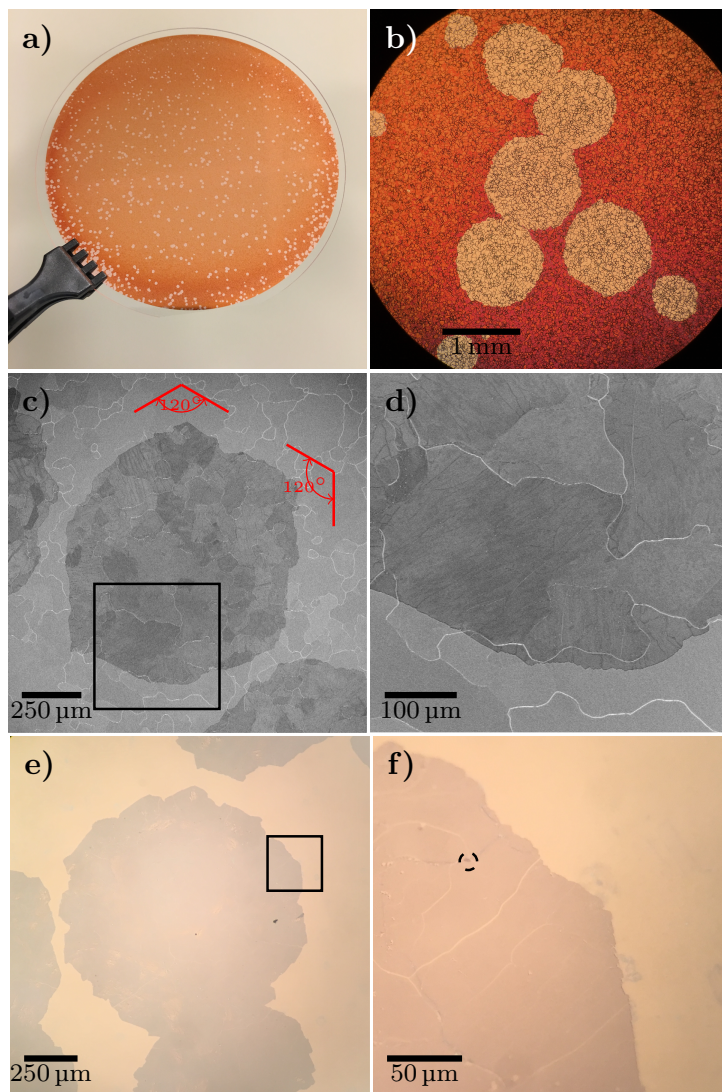


Figure 6.11: Millimeter-size GDs grown on 1200 nm-thick Cu film. a) Photograph of a 3-inch Cu/quartz wafer after a 30 min graphene growth. b) Optical microscope image of mm-size GDs as grown on Cu film. c) In-lens SEM image of a GD as-grown on Cu. d) Higher magnification image corresponding to the framed area in (c). e) Optical microscope image of GDs transferred on a 90 nm-thick SiO₂/Si substrate. f) Higher magnification corresponding to the framed area in (e). The dashed circle shows a small bilayer dot.

Although the Cu film's intrinsic high purity and smooth surface morphology may contribute to the suppression of nucleation sites, the successful growth of compact large-area GDs mainly results from the appropriate adjustment of the CVD conditions inside the furnace during the CVD process.

Further characterization is achieved by transferring as-produced graphene from the Cu film onto 90 nm-thick SiO₂/Si wafers. In order to evaluate the structural quality and number of layers, Raman spectroscopy measurements have been performed on the two transferred GDs presented in Fig. 6.12.

Figure 6.12b displays stacked Raman spectra corresponding to the different locations identified by colored dots in Fig. 6.12a. These spectra were acquired using a 2400 grooves/mm-grating in order to obtain precise values of the peak positions and full width at half maximum (FWHM). Each spectrum exhibits a 2D peak (with a position varying from 2670 to 2690 cm⁻¹), a G peak (1577-1582 cm⁻¹) and a very weak D peak (1337-1341 cm⁻¹) which suggests an insignificant amount of structural defects. The intensity ratio I_{2D}/I_G about 2, the relatively narrow 2D peak, and the fact that the 2D peak can be fitted by one single Lorentzian component indicate that the GDs is monolayer [154,158]. The observed shift of the peaks is more likely due to mechanical stress and/or doping induced by the transfer process steps (as explained in chapter 3).

To further assess the spatial uniformity of graphene quality and thickness within a single GD, Raman mappings have been acquired on 50×60 μm² areas located in the center and at the periphery of the GD as shown by the insets in Fig. 6.12a. Regardless of whether the mapping is acquired at the periphery (Figs. 6.13) or at the center (Figs. 6.14), the intensity of the D peak is almost 2 orders of magnitude smaller than the one of the G peak (except in the transfer process-induced cracks that are visible in the insets of Fig. 6.12a). Both mappings also exhibit a 2D to G intensity ratio ranging from 1.7 to 2.5 which suggests the absence of bilayers regions in these locations.

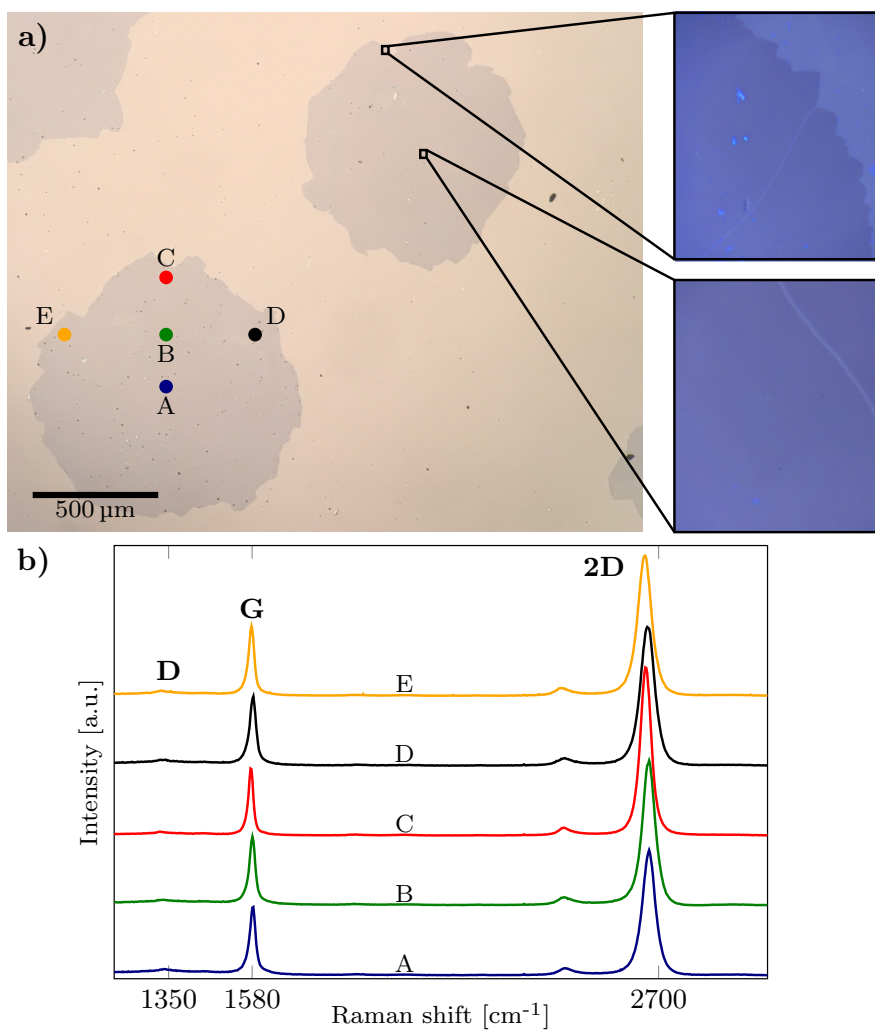


Figure 6.12: Raman measurements of graphene domains. a) Optical microscopy image of graphene transferred onto a 90 nm-thick SiO_2/Si wafers. Insets are higher magnification images of the small square areas in (a). b) Raman spectra acquired in the different locations denoted by color dots in (a).

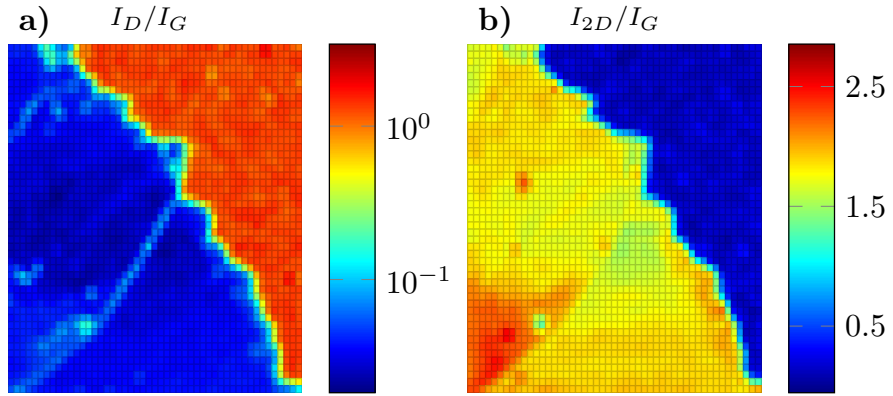


Figure 6.13: I_{2D}/I_G and I_D/I_G Raman mappings taken along the graphene domain edge shown in the insets of Fig. 6.12.

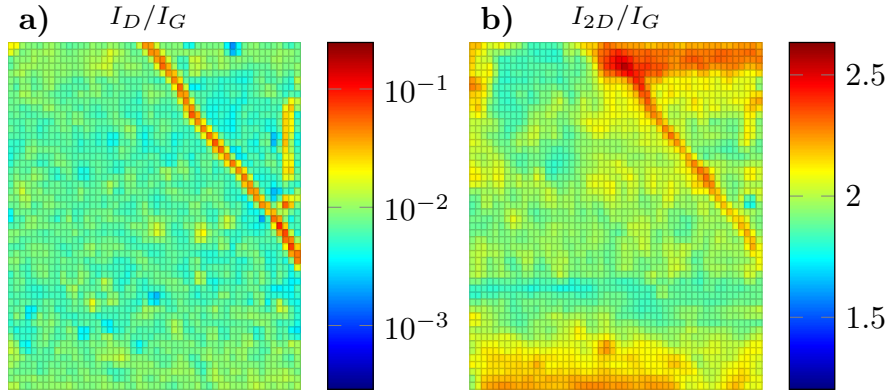


Figure 6.14: I_{2D}/I_G and I_D/I_G Raman mappings taken at the center of the domain shown in the insets of Fig. 6.12.

Raman coherent information and hence, uniform graphene quality and thickness over the GD surface demonstrate a good consistency in the growth conditions as the GD formation proceeds. This confirms our above-mentioned observations stating that even if the GDs shapes are not completely hexagonal, individual mm-size graphene domains originate from a single graphene nucleus.

Figure 6.15 shows the full width at half maximum of the 2D band corresponding to the surface areas shown in the insets of Fig. 6.12. The spatial variation of the $FWHM_{2D}$ suggests that there is a spatial variation of strain and probably a variation of doping within the probed surface areas (see chapter 3). The strain and doping are most likely induced by the transfer process which traps impurities at the graphene/ SiO_2 interface, does not uniformly deposit graphene on the underlying substrate (which is not atomically smooth) and causes local lattice deformations.

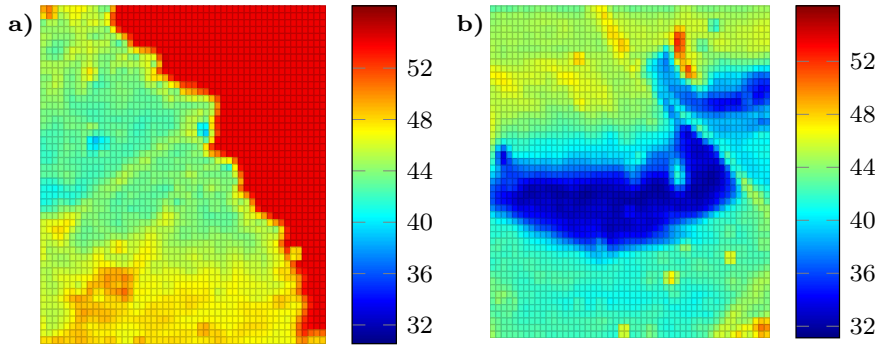


Figure 6.15: $FWHM_{2D}$ Raman mappings taken (a) along the GD edge and (b) at the center of the domain as shown in the insets of Fig. 6.12.

6.9 Conclusions

In conclusion, we developed a new CVD approach to produce single-layer graphene sheets with mm-size graphene domains on thin Cu films. This innovative approach is based on the continuous regulation of global pressure inside the furnace during the CVD synthesis protocol. Adjusting the global pressure allowed us to find optimal conditions for both the Cu annealing/ramping and the graphene nucleation/growth steps. Our findings suggest that the global pressure during graphene growth does not play a major role in determining the nucleation site density and hence the maximum dimensions of graphene domains. However, using high pressure levels is a key graphene growth condition to yield defect-free graphene domains with compact shape and smooth edges. On the other hand, we observed that annealing the Cu substrate in an Ar atmosphere is essential to obtain large area graphene domains and higher Ar pressure conditions favor a low density of nucleation sites. Finally, we found out that evacuating the CVD furnace for 5 min prior to graphene growth is an effective way to address the dewetting issues observed when a high pressure of Ar is used during the Cu annealing step. Thanks to these considerations, we are able to routinely produce millimeter-size single-crystals of graphene on a thin Cu film which is a more suitable platform than Cu foils for the implementation of graphene based practical applications.

Chapter 7

Synthesis Results on Copper Foils

Chapter 6 demonstrated that the nucleation site density of graphene could be tuned over almost 3 orders of magnitude by simply adjusting the Ar pressure level into the CVD furnace during the Cu annealing step. This observation was attributed to the reduction of the carbon concentration present on the Cu surface prior to the graphene growth induced by traces amounts of oxygen in Ar. This chapter further explores the impact of the Cu annealing conditions on the subsequent formation of graphene. To explore a wider range of conditions, the CVD furnace has been connected to an additional gas line which can deliver a precise amount of oxygen regardless of the global pressure. In the same vein, graphene growth is performed using Cu foils instead of Cu films in order to take advantage of their higher robustness to high-temperature long-duration Cu annealing processes.

After presenting the motivations for this study in section 7.1, section 7.2 focusses on systematically comparing the relative effectiveness of various Cu annealing conditions in reducing the nucleation site density. Section 7.2 also provides a series of additional experiments aiming to better understand the underlying mechanisms. Then, section 7.3 presents how the in-situ thermal treatment impacts the formation of additional layers underneath the large single-crystalline domains. Finally, the last section outlines the main findings discovered in this study.

7.1 Motivations

The work described in this chapter has been motivated by a few scientific questions and considerations:

Up to now, different research groups demonstrated the production of graphene single-crystals with lateral dimensions exceeding a few millimeters on Cu foil (see tables in chapter 2). These results were achieved through the combined use of different (i) catalytic ex- and in-situ substrate treatments, (ii) CVD conditions, (iii) complex Cu substrate geometries and, (iv) particular CVD furnace configurations. Such wide variety of CVD procedures makes it challenging to really appreciate the actual relative effectiveness of reported Cu foil treatments in controlling the nucleation site density. Rigorously evaluating the effectiveness of Cu thermal annealing processes reported in the literature can offer relevant guidelines for the optimization of the graphene synthesis procedure.

Chapter 6 along with other reports demonstrated that oxidizing, in a way or another, the Cu catalyst was essential to produce large graphene domains. However, the underlying mechanism responsible for decreasing the nucleation site density is subject to a great deal of debate and there are significant discrepancies in the explanations proposed in the literature. Gaining more insight about the actual role of oxygen in the complex graphene growth mechanism is of great interest in the quest towards the growth of high-quality giant graphene domains.

Most of the literature focused on improving the nucleation site density in order to eventually produce large-area domains. However, the impact of the Cu foil thermal treatment on the formation of additional layers during the subsequent graphene growth step has not been addressed yet.

Chapter 6 also demonstrated the great potential of the pressure-controlled CVD system in decoupling the influence of the Cu annealing conditions from the one of the graphene growth conditions on the graphene formation. The pressure-controlled CVD system can be further exploited to rigorously investigate a wide range of Cu annealing conditions including different pressure regimes and various gas compositions while using identical graphene growth conditions.

Finally, the major advances in the field of graphene growth have been developed using Cu foils as catalyst. Using Cu foils in this work can be helpful to put the obtained results into context with those published in the literature. Moreover, we can take advantage of a more robust Cu substrate for the long-duration high-temperature oxidizing conditions.

7.2 Nucleation site density

In order to evaluate how graphene growth is affected by the in-situ Cu foil treatment conditions, different series of CVD experiments have been carried out with varying Cu annealing conditions while keeping identical graphene growth steps. An identical CVD growth step throughout the various experiments, which is essential to ensure the adequacy and scientific rigorousness of this comparative study, has been achieved using the pressure-controlled CVD setup.

7.2.1 Cu annealing during the high temperature plateau

Figure 7.1 shows the temperature, pressure and gas flow profiles that have been employed for the different steps involved in the CVD protocol, i.e. CVD furnace warming up, Cu annealing, graphene growth and furnace cooling down.

In order to limit the impact of the conditions used during the one hour-long CVD warming step and ensure that graphene growth behavior is predominantly dictated by the Cu annealing step conditions, it has been decided to heat up the CVD furnace under a low pressure (1 mbar) of an inert gas (pure Ar). Once the furnace reaches the growth/annealing temperature (T_{gr}), the annealing gas (pure Ar, Ar/H₂ or Ar/O₂ mixtures) is injected in the CVD furnace and the metering valves between the CVD furnace and the pumping system are adjusted to achieve the desired global pressure. Two different pressure regimes are considered in this work: a low pressure (LP) and a near-ambient pressure (NAP) regime thereby mimicking low pressure (LPCVD) and ambient pressure (APCVD) growth processes reported in literature. The global pressure

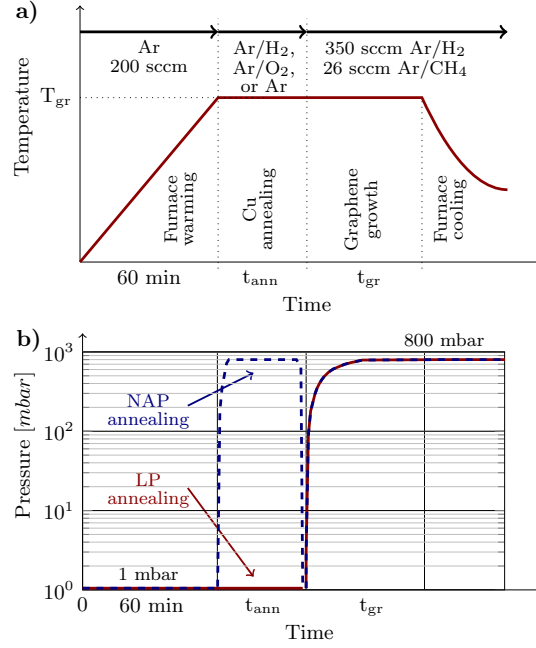


Figure 7.1: (a) Gas flow, temperature and (b) global pressure profiles used for the CVD experiments carried out to study the impact of Cu annealing pressure and gas composition on graphene nucleation site density. Solid red and dashed blue pressure profile lines correspond to the CVD protocols with a LP and a NAP pressure annealing step, respectively.

of the NAP regime is set to 800 mbar in order to maintain the proper sealing of the LPCVD set-up. Once the Cu annealing step is completed, the CVD furnace is purged (the pressure drops down to 1 mbar) before injecting Ar/CH₄ (26 sccm, 2000 ppm in Ar) and Ar/H₂ (350 sccm, 10% in Ar) gas mixtures to start graphene nucleation and growth. This process step ensures that regardless of the gas composition or global pressure employed during the Cu annealing step, the graphene growth step will be achieved under the exact same conditions, that is with identical global pressure, partial pressures of methane and hydrogen-to-methane ratio profiles. The graphene growth step is performed under a pressure

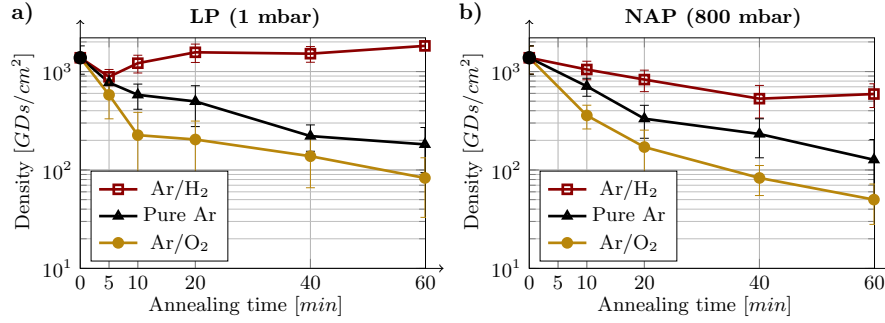


Figure 7.2: Evolution of the graphene domain density as a function of the gas composition and the annealing duration (t_{ann}) for high temperature annealing steps performed under (a) low pressure and (b) near-ambient pressure, as described in Fig.7.1.

of 800 mbar as it yields graphene domains with a more compact shape and smoother edges and also reduces Cu foil evaporation loss (as explained in chapter 6) [75,194]. In order to produce isolated graphene domains that can be individually observed and counted and hence, obtain an estimation of their shape, size and density, the graphene growth step duration (t_{gr}) has been adjusted for each CVD experiment. Details about the CVD experiments can be found in Ref. [116].

Figures 7.2a and 7.2b show the evolution of the graphene domain density as a function of Cu annealing duration (ranging from 0 to 60 min) for both LP and NAP regimes and different gas atmosphere compositions. Given the strong affinity of copper for oxygen, particular precautions have been taken while annealing the Cu substrate under the Ar/O₂ atmosphere. It appeared essential to maintain a relatively low partial pressure of oxygen in the CVD furnace in order to avoid excessive Cu oxidation during the annealing step that would eventually lead to the degradation of the Cu foil physical integrity upon the reducing treatment caused by the subsequent graphene growth step. In order to maintain a relatively smooth Cu surface and avoid any Cu foil damage, the oxygen gas feedstock dilution has been chosen to be 1% O₂ and 500 ppm O₂

in Ar for the LP and NAP Cu treatments, respectively (more details can be found in Ref. [116]). Starting graphene growth directly after the furnace warming step ($t_{\text{ann}}=0$ min) yields a graphene domain density of about 1400 GDs/cm². This represents about a 200-fold improvement compared with the graphene density that would have been obtained using 200 sccm of Ar/H₂ instead of Ar in the warming up step (data not shown) which is consistent with chapter 6 and previous works [85]. When performed under a hydrogen-free atmosphere, the high temperature Cu foil annealing step effectively contributes to decrease the nucleation site density as the number of GDs has been reduced by at least one order of magnitude after one hour. On the other hand, annealing the Cu foil under a reducing atmosphere composed of 10% of hydrogen has a mixed influence on the graphene domain density. The Ar and Ar/O₂ trends suggest that extending the Cu annealing duration beyond 1 hour would further reduce the nucleation site density and annealing under near-ambient pressure has a potentially greater beneficial effect than annealing under low pressure.

7.2.2 Cu annealing during the CVD furnace warming

As extending the high temperature Cu annealing step over a few hours is time and energy consuming and in turn, does not represent a viable strategy for the industrial production of graphene, it is preferable to rather take advantage of the CVD furnace warming step. In order to disclose the potential of the one-hour long heating step in decreasing the domain density, a series of CVD experiments have been carried out using identical graphene growth conditions as previously shown in Fig. 7.1 but without the high temperature Cu annealing plateau. Given that the NAP Cu annealing regime yields better results, the warming step has been performed at a global pressure of 800 mbar with varying oxygen dosing. The oxygen dosing has been controlled by diluting the Ar/O₂ gas feedstock with pure argon in order to achieve oxygen concentrations in the atmosphere of 32.5, 62.5, 125, 250 and 500 ppm (see Ref. [116]). Figure 7.3 shows the evolution of the graphene domain density with the increase of oxygen concentration inside the CVD furnace.

When comparing Fig. 7.3 with Fig. 7.2, it can be noted that performing the heating step under an argon atmosphere of 800 mbar instead of 1 mbar does not significantly improve the graphene domain density (about 1112 instead of 1381 GDs/cm² on average). It can also be observed that the graphene domain density rapidly saturates to about 300 GDs/cm² which is more than the density values obtained when using an additional Cu annealing step.

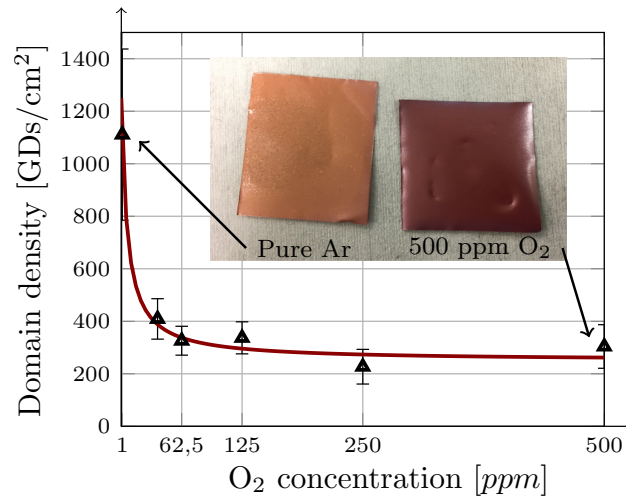


Figure 7.3: Evolution of the graphene domain density as a function of the O₂ concentration of the gas phase during the 1-hour long warming step performed under a global pressure of 800 mbar. The photograph in the inset shows Cu foils that have been annealed and directly cooled down without performing the graphene growth step.

The photograph in the inset of Fig. 7.3 and in the optical microscope images in Fig. 7.4 show that using an inert (pure Ar) or oxidative atmosphere (Ar/O₂ mixture) both result in the growth of a Cu oxide layer on the catalyst surface. This oxide layer, that gives the surface a matte pinkish or purplish tint depending on its thickness, is mainly composed of Cu₂O as identified by Raman spectroscopy and reported in the literature [195, 196].

The formation of a thick Cu oxide layer on the catalyst surface (~ 50 -90

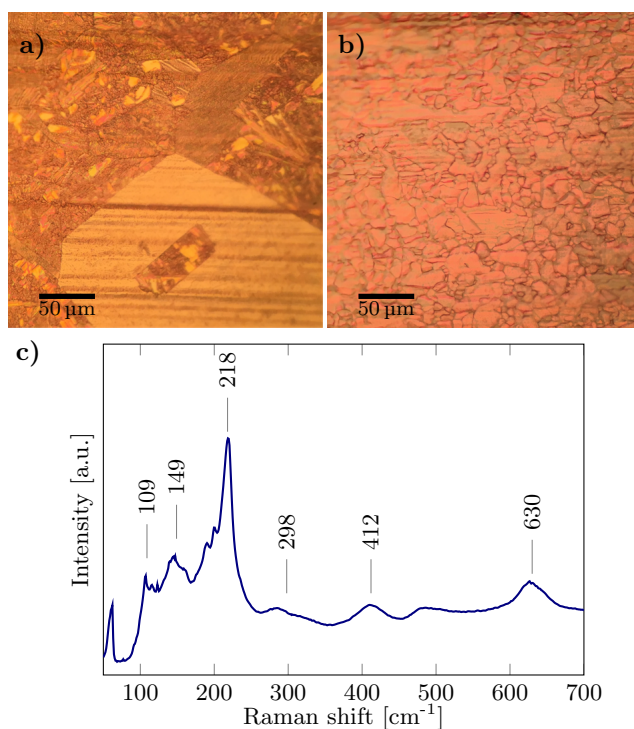


Figure 7.4: Optical microscope images taken on the Cu foil surface after a 1-hour long warming step under a pressure of 800 mbar using (a) a pure Ar or (b) an Ar/O₂ (500 ppm) atmosphere. Images (a) and (b) correspond to the photograph in the inset of Fig. 7.3. c) Raman spectrum acquired on the Cu oxide layer exhibiting the Cu₂O main Raman features.

nm and ~ 1.1 - $1.5 \mu\text{m}$ for Ar and Ar/O₂, respectively) indicates that the bulk of the Cu foil is saturated in oxygen (i.e. it absorbed a quantity of oxygen beyond its solubility limit) for both "pure Ar" and Ar/O₂ atmosphere. The formation of a Cu oxide layer upon the high temperature exposure to "pure Ar" atmosphere is easily observable when the warming step is performed under 800 mbar and less evident when performed under 1 mbar. Such observation indicates that the oxygen residual concentration in the Ar feedstock (about 1 ppm according to

Praxair) is either not sufficient to saturate the Cu foil in oxygen or that the Cu oxide layer evaporation (enhanced at 1 mbar) prevails over its formation.

Exposing the Cu foil to oxygen only during the warming ramp (see Fig. 7.3), even with a relatively high concentration (500 ppm at 800 mbar), does not yield better domain density results than exposing it for one hour at high temperature under a low pressure of "pure Ar" or Ar/O₂ gas mixture (see Fig 7.2). This result evidences that the reduction of the nucleation site density depends on the oxygen concentration in the atmosphere but also strongly depends on the temperature and time of exposure. Graphene domains with lateral dimension exceeding a few millimeters without prolonged Cu annealing step has been achieved by combining favorable conditions during both the furnace warming and the Cu annealing 1-hour long steps. Heating the CVD furnace under 800 mbar of Ar and then annealing the Cu substrate under Ar/O₂ (800 mbar, 1050 °C, about 100 ppm O₂) yields a density of about 16 GDs/cm² that, after a 2-hour growth duration, turn into graphene domains with lateral sizes of about 2-3 millimeters as shown in Fig. 7.5

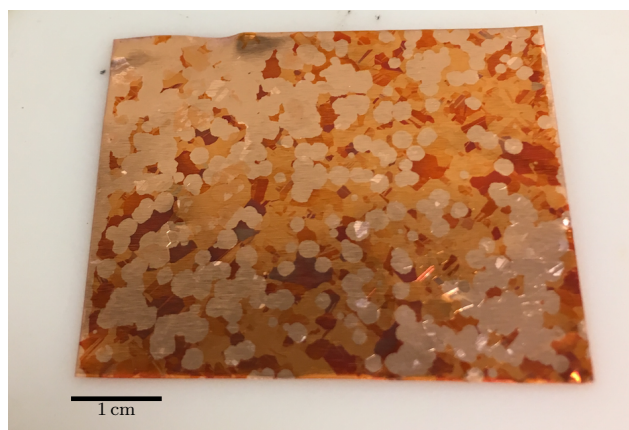


Figure 7.5: *Photograph of a Cu foil with graphene domains exhibiting lateral dimensions of about 2-3 mm.*

7.2.3 Role of oxygen: discussion and results

The benefits of using oxygen prior to graphene growth has been observed in several recent studies. These studies either intentionally pre-oxidized the Cu catalyst in air prior to loading it into the CVD furnace [87, 90, 97, 180, 188, 197], employed an inert atmosphere to maintain Cu native oxide on the catalyst surface [85, 114, 180] or directly introduced oxygen in the furnace prior to the graphene growth step [100, 102, 103, 111, 198, 199]. Although it is clear that oxygen is a key process parameter to obtain large graphene domain, the exact mechanism responsible for decreasing the nucleation site density is subject to a great deal of discussion and debate.

Most of the explanations that have been proposed in the literature concern a modification of the Cu surface including: (i) the passivation of active sites for nucleation by adsorbed oxygen [102], (ii) the presence of catalytic inactive Cu_2O on the surface at the onset of graphene growth [85, 114, 199], (iii) the formation of Cu nanoparticles acting as a finite number of nucleation sites [113], (iv) the reduction of Cu surface contamination [87, 188, 198], (v) the rearrangement of the Cu structure into a less active surface [104], (vi) the Cu catalyst surface roughness improvement [180], (vii) the "oxygen gettering" of out-diffused bulk defects [197], and (viii) the presence of a Cu oxide passivation layer during the Cu warming/annealing step to prevent active C species accumulation prior to graphene growth [138].

On the other hand, a few other research groups claimed that the effect of oxygen is not only limited to the Cu foil surface but is also linked to the Cu foil bulk [90, 97, 103]. They attributed the reduction of nucleation density to the decarburization of the Cu foil (which has also been referred to as oxidative carbon removal, carbon scavenging or carbon depletion) induced by oxygen when it diffuses in the copper foil and reacts with dissolved carbon. The wide variety of interpretations probably arises from the different approaches that have been employed to expose the Cu foil to oxygen, the wide diversity of graphene growth protocols as

well as the complexity of the mechanisms by which oxygen contributes to reducing the nucleation site density. It is thus very likely that the actual role of oxygen is a combination of the aforementioned proposed mechanisms.

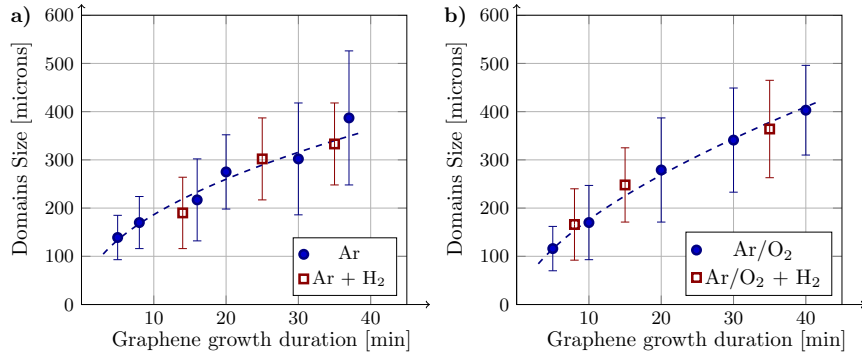


Figure 7.6: *Evolution of graphene domain lateral size with graphene growth duration (t_{gr}). Blue dots: Graphene domains grown after a 20-min long Cu annealing step performed under an atmosphere of (a) Ar or (b) Ar/O₂. Red dots: graphene domains grown after an additional annealing of 15 min under an Ar/H₂ atmosphere to completely reduce the Cu oxide layer prior to graphene nucleation.*

In order to better understand how involving oxygen prior to graphene growth reduces the nucleation site density and to determine which mechanisms prevail in the case of an in-situ Cu foil oxidation, another series of CVD experiments has been carried out. These CVD experiments consist of annealing the Cu foils at 800 mbar for 20 min (at $T=T_{gr}$) under either "pure Ar" or Ar/O₂ (500 ppm) gas mixture and observing the evolution of graphene domain lateral size as a function of the graphene growth step duration (see Ref. [116] for the CVD parameters details). The lateral size of as-grown graphene domains using the Ar and Ar/O₂ Cu annealing steps are displayed in Fig. 7.6a and Fig. 7.6b, respectively (blue dots). The progressive slowdown of graphene growth rate is likely to be caused by the increasing graphene coverage of Cu surface area and the

corresponding reduction of active surface available for methane surface catalysis. The data point regression tends to show that graphene domains already have a finite size at the onset of the graphene growth step. This offset arises from the fact that methane and hydrogen keep flowing into the CVD furnace during the cooling step and graphene domains keep developing for a few minutes. It can be observed that graphene domains grown after the "pure Ar" annealing exhibit similar lateral dimensions compared with those grown after the Ar/O₂ annealing while this latter produced an oxide layer on the catalyst surface about 20 times thicker ($\sim 3\text{ }\mu\text{m}$ in contrast to $\sim 140\text{ nm}$). This observation suggests that a thicker oxide layer does not induce a more pronounced catalyst surface passivation or does not delay the graphene formation.

To further investigate if the reduction of the nucleation site density arises from the direct interaction of a Cu oxide layer (Cu₂O) with the onset of graphene formation, similar experiments have been conducted but an additional 15-min long annealing step has been performed under an Ar/H₂ atmosphere (800 mbar, 10% hydrogen in argon) to make sure that the Cu oxide layer is reduced before the onset of graphene formation. The resulting graphene domain lateral dimensions (displayed by red squares in Fig. 7.6a and 7.6b), seem to fit pretty well with the previous experiments in which graphene was grown directly after the oxidative step. Similar results obtained with or without the Cu oxide layer advocates that the oxide layer does not play the role of a passivation layer for the nucleation of graphene. It is believed that the high partial pressure of hydrogen present in the CVD atmosphere during the graphene growth step (resulting from NAP CVD conditions and a high H₂-to-CH₄ ratio) reduces the Cu oxide surface layer before the catalytic decomposition of methane generates enough C-based species on the Cu surface to initiate graphene formation.

These results however do not rule out the possibility that the oxide layer or dissolved oxygen in the Cu bulk might play a role in graphene growth as it has been claimed in recent works [85, 102, 199]. Indeed, as the Cu oxide layer reduction and dissolved oxygen removal rates are strongly

dependent on the arrival rate of hydrogen on the Cu surface at the onset of graphene growth, graphene growth processes performed under low pressure and low H_2 -to- CH_4 ratio conditions are potentially more sensitive to the oxygen content of catalyst.

It is also believed that the Cu surface roughness modification upon the high temperature annealing does not play a major role in determining the nucleation site density either. Although annealing the Cu foil under a high global pressure level helps maintaining the Cu vapor close to the solid Cu surface and physically improves the Cu surface morphology through an evaporation/re-deposition process, this approach does not effectively remove the macro/microscopic features of the cold-rolled Cu foils such as rolling striations and other Cu surface singularities (see Ref. [116] for surface profilometry data) [81, 107, 194, 200].

It also appears that the Cu surface oxidation and subsequent reduction upon the reducing graphene growth atmosphere do not particularly remove the surface microscopic features and do not improve the Cu surface roughness, regardless of the global pressure level. Given the importance of Cu sublimation and the constant Cu microstructure evolution that take place at such high temperatures, it is challenging to experimentally appreciate the actual influence of Cu annealing conditions on the Cu surface morphology prior to graphene growth. In order to get some insight into the influence of Cu annealing conditions on the Cu surface morphology, the Cu surface has been analyzed using AFM and SEM after performing the Cu annealing described in Fig. 7.1 (1-hour-long plateau at 1050 °C) followed by a 10-min-long reduction step before cooling down the samples. Figure 7.7 shows SEM images of the Cu surface for Cu samples annealed under Ar/H_2 and Ar/O_2 atmosphere under both LP and NAP regimes.

AFM images presented in Fig. 7.8 provide a more extensive information about the Cu surface morphology. Unfortunately, it is very challenging to know how the surface roughness plays a role in the nucleation site density for 2 reasons. First, it is difficult to probe the Cu surface morphology in-situ just before starting the graphene growth step and realize

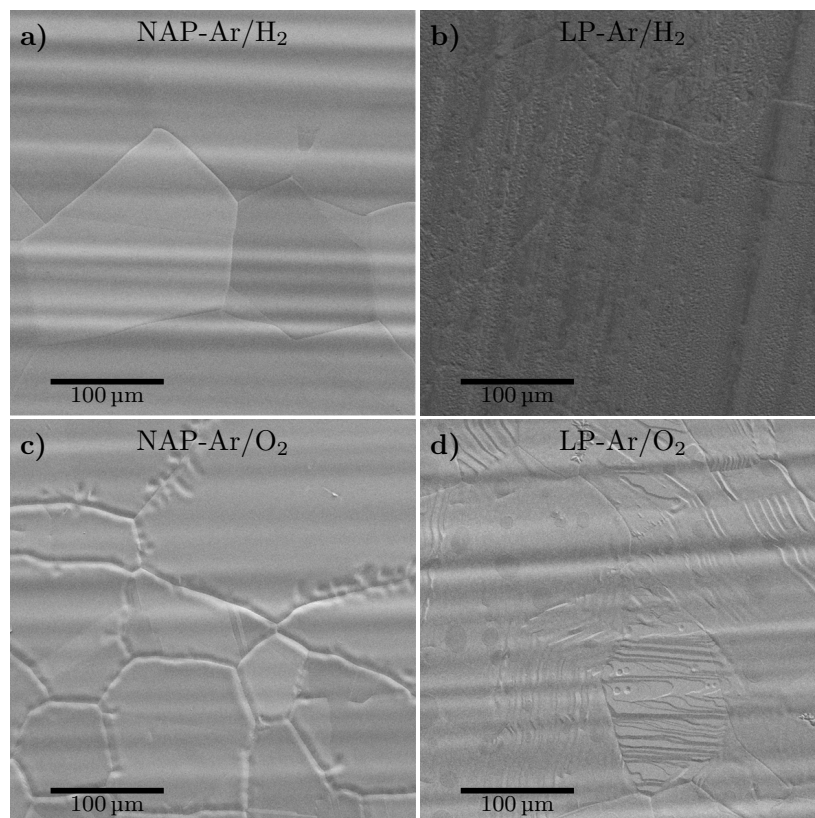


Figure 7.7: Impact of Cu annealing conditions on the Cu surface morphology. E-T SEM images of the surface of Cu foil samples resulting from a 1-hour-long Cu annealing step at 1050 °C followed by a 10-min-long exposure to Ar/H₂ to reduce the Cu oxide layer present on the surface. The global pressure and gas composition conditions employed for each Cu annealing process are displayed on the top of each image.

which kind of Cu surface morphology singularities/features will act as preferential sites for the nucleation of graphene domains. Measuring ex-situ the Cu surface morphology using AFM only gives a very rough estimation of the Cu surface morphology (given that the cooling process modifies the surface morphology). Second, there does not seem to be a correlation between the Cu surface morphology and the location of graphene domains. In other words, graphene domains that are observed on the Cu surface do not seem to have nucleated in specific locations such as Cu grain boundary grooves, cold-rolling striations, Cu surface singularities, etc (see Fig. 7.12).

As the best Cu surface roughness (obtained upon an annealing under 800 mbar of Ar/H₂) does not match the best results in terms graphene domain density, it seems unlikely that the surface roughness represents the key factor for controlling the nucleation site density.

It is thus believed here that the nucleation site density is controlled by the concentration of carbon present in the Cu foil bulk and on its surface at the onset of the graphene growth step. Using a reducing atmosphere during the warming and Cu annealing steps would maintain the Cu surface catalytically active and probably cause the catalytic reaction of adventitious carbonaceous gas molecules on the Cu surface during the heating and annealing steps as any carbon contaminations present in the CVD furnace are prone to desorb, pyrolyze and be transported in the gas mainstream. As explained in chapter 6, the contamination may come from an initial surface contamination produced by the Cu foil manufactory, can be brought through handling during the CVD furnace loading, from the inevitable leakage rate in the mass flow controllers of methane or even from previous CVD runs that deposited graphene and amorphous carbonaceous species on the CVD inner walls assisted by Cu vapor evaporation re-deposition as previously explained in chapter 6.

Given that the solubility of carbon in Cu exponentially increases with temperature (about 8 at. ppm at 1050 °C), the carbon content of the Cu foil can greatly raise prior to graphene growth [58]. Introducing oxygen inside the furnace has a dual role as it passivates the Cu surface prior

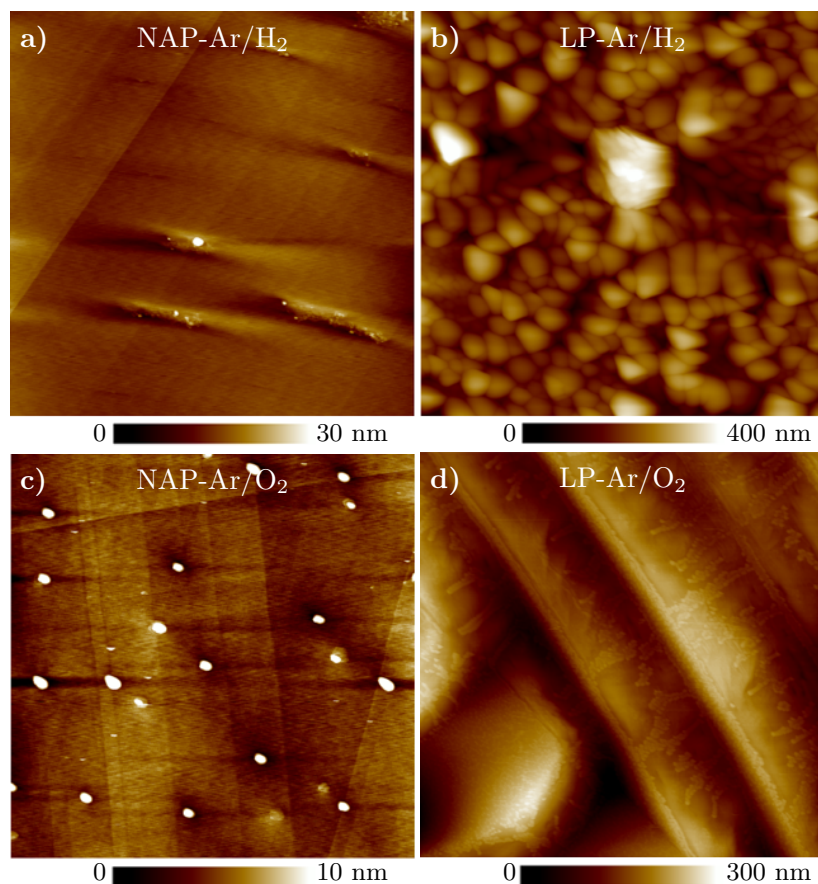


Figure 7.8: Impact of Cu annealing conditions on the Cu surface morphology. AFM images of the surface of Cu foil samples resulting from a 1-hour-long Cu annealing step at 1050 °C followed by a 10-min-long exposure to Ar/H₂ to reduce the Cu oxide layer present on the surface. The lateral size of the scanned areas is 5 μm for images (a), (b) and, (c) and 10 μm for image (d). The global pressure and gas composition conditions employed for each Cu annealing process are displayed on the top of each image.

to graphene growth which prevents any increase of the carbon content during the warming and annealing steps and contributes to reducing the original amount of carbon on the Cu surface, in bulk of the foil and probably inside the CVD furnace through the oxidative carbon removal. In order to verify that the introduction of O_2 inside the CVD furnace during the Cu annealing step contributes to reducing the carbon content of the Cu surface, X-ray photoelectron spectroscopy (XPS) measurements have been performed on different Cu foils samples: as-received, annealed under Ar/H_2 , annealed under Ar/O_2 and after the growth of individual graphene domains (see Ref. [116]). XPS results show that the surfaces of as-received Cu foils and Cu foils annealed under Ar/H_2 contain a higher C concentration than Cu foils annealed under Ar/O_2 . Interestingly, the concentration of C measured on the surface of Cu that has been annealed under Ar/O_2 and subsequently exposed to graphene growth conditions for 40 min is inferior to the concentration of Cu foils as-received and annealed under Ar/H_2 . These results indicate that the initial amount of C present on the as-purchased Cu foils is rather high compared to the C concentration present during the graphene growth step and that annealing the Cu foils under an oxygen-containing atmosphere efficiently contributes to reducing this C concentration on the surface.

The dependency of the obtained graphene domain density on the O_2 exposure temperature and duration can be explained by the enhanced solubility of oxygen in the Cu lattice at high temperature (about 270 ppm at 1050 °C) and the diffusion rate of CO and CO_2 gas molecules through the bulk of the Cu foil at high temperature [201]. Although gaseous carbon oxides are spontaneously generated (and preferably formed over Cu_2O as thermodynamically more stable [202]), these molecules have to diffuse out of the Cu foil by going through the Cu foil thickness and the freshly produced Cu oxide surface layer. The rate of carbon removal is thus probably controlled by the CO/ CO_2 gas molecules out-diffusion rather than the absorption of oxygen. When using "pure" argon during the pre-growth thermal treatment (see Fig. 7.2 and 7.3), the trace amounts of oxygen present in the gas feedstock are likely to be the main contributor responsible for the reduction of the nucleation site density. The NAP Cu annealing regime yields slightly better nucleation results

than the LP regime (see Fig. 7.2) because it provides a higher partial pressure of oxygen which better contributes lowering the carbon content of the catalyst.

In the absence of oxygen in the Cu annealing atmosphere, the oxidative carbon removal does not represent the major mechanism controlling graphene nucleation. The mixed effect of annealing the Cu foil under an Ar/H₂ atmosphere can be explained by two other phenomena. First, hydrogen can also contribute to reducing the carbon concentration present on the Cu foil surface or dissolved into the bulk C_(s) through the chemical reaction $C_{(s)} + 2 H_{2(s)} \rightarrow CH_{4(g)}$ [203]. Using a higher global pressure and hence a higher partial pressure of hydrogen would make the carbon removal process prevail over the catalysis of undesired carbonaceous molecules on the Cu surface and thus reduce the nucleation of graphene. The physical smoothing of Cu surface upon the high temperature annealing under high pressure could also be a major reason explaining why the NAP annealing yields better results than the LP regime in absence of oxygen.

7.3 Graphene domain thickness

In addition to playing a crucial role in controlling graphene nucleation site density, the Cu annealing step also influences the thickness of growing graphene domains. In order to observe its effect, graphene domains obtained after the 1-hour long Cu annealing processes described in Fig. 7.1 have been transferred onto 300-nm-thick SiO₂/Si substrates and observed with optical microscopy (see Fig. 7.9).

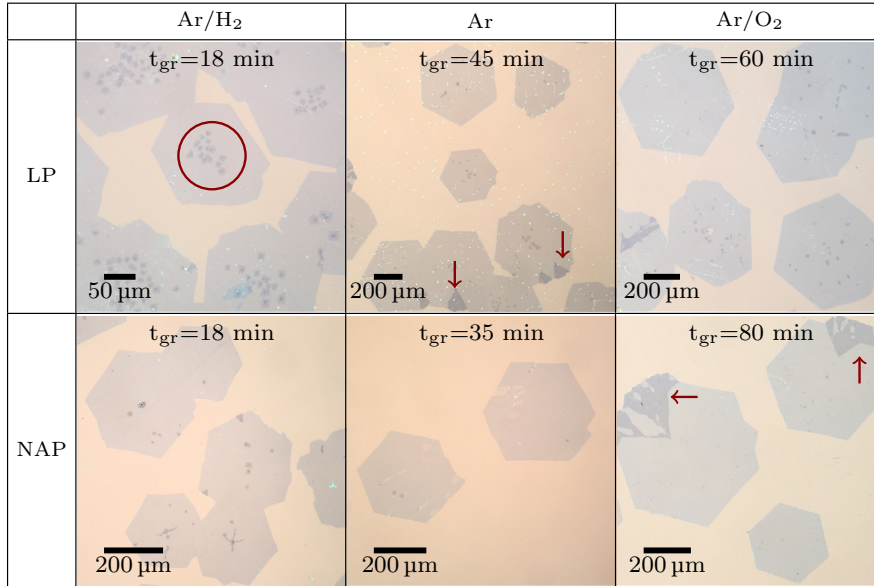


Figure 7.9: Optical images of graphene domains obtained after 1-hour long Cu annealing (presented in Fig. 7.1) and transferred on a SiO₂ substrate. Graphene growth durations (t_{gr}) has been adjusted in order to avoid the coalescence of graphene domains. Two different kind of multi-layer graphene regions are pointed out using a red circle (round-shaped MLRs) and arrows (branch-like MLRs).

When annealed under a reducing atmosphere (Ar/H₂), graphene domains are predominantly single-layer and feature some compact bi- or few-layer graphene regions with lateral dimensions of about 10 micrometers and located in the vicinity of their center (see red circle in

Fig. 7.9). When annealed under a hydrogen-free atmosphere (Ar or Ar/O₂), graphene domains exhibit two different kinds of multi-layer regions (MLRs): the round-shaped compact regions as aforementioned and other occasional regions with more complex shapes suggesting that it has been grown radially along with the first graphene layer (as pointed out with red arrows in Fig. 7.9).

7.3.1 Round-shaped multi-layer regions

It is found that the round-shaped MLRs (shown in Fig. 7.9) are not uniformly distributed over the entire graphene sample as they are quasi absent in the center of the Cu/graphene sample and present in large numbers at its periphery (about a few millimeters from the Cu sample edge). The location dependency of this kind of MLRs suggests that their formation is caused by the exposure of the Cu foil backside to the methane/hydrogen gas mainstream during the graphene growth step. Methane molecules can react at the Cu foil backside, produce carbon based species that are dissolved into the Cu foil bulk and able to diffuse through the thickness to the Cu top surface to form extra layers underneath the first growing graphene single-crystalline domain. Given that the Cu annealing step is performed at a temperature close to the melting point of the catalyst ($\sim 1084^{\circ}\text{C}$), the Cu foil softens and tends to conform to the flat quartz wafer used as support. Due to the small space at the interface between the Cu foil and the quartz wafer, the methane molecules have a limited diffusion length and cannot react on the Cu surface in the center of Cu foil backside when its dimensions exceed a few centimeters square.

This phenomenon is evidenced in Fig. 7.10 which shows the topside and the backside surfaces of a $5\times 5\text{ cm}^2$ Cu foil after the growth of graphene. Large graphene domains have only been able to grow on the periphery of the Cu foil backside. It is very likely that the small graphene domains (with dimensions of maximum a few hundreds of micrometers) present at the center of the Cu foil backside have been grown from active C species that have been generated on the Cu topside surface and which have been able to diffuse through the Cu foil thickness.

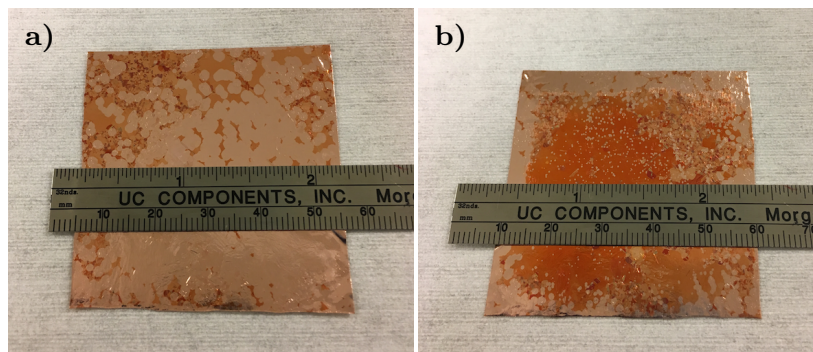


Figure 7.10: Photographs of a Cu foil after the graphene growth process and a slight Cu oxidation step to make mm-size graphene domains visible. a) Cu foil top surface. b) Cu foil backside.

Round-shaped multi-layer graphene regions have been obtained on the entire Cu surface by suspending the Cu foils (for example by bending them to form an arch when loading them in the furnace or simply using a thicker Cu foil (100 micrometer-thick) that does not soften as much as the 50 micrometer-thick foils) or suppressed over extended regions by using larger Cu samples that will be in close contact with the support and prevent the methane molecules to diffuse at the fused quartz/Cu foil backside interface. This finding is consistent with previous experimental studies that either witnessed the formation of multi-layer graphene outside Cu foil enclosures caused by surface reaction at the inside or suppressed the formation of multi-layer graphene by employing a "gettering" support for the foil to shut down the carbon supply at the Cu foil backside [122, 185, 204–206].

As a consequence, this kind of MLRs seems to be more related to the Cu configuration rather than the CVD protocol as it is observed regardless the atmosphere composition or pressure regime that has been employed during the Cu annealing/warming steps. However, it is found here that their lateral size, thickness and density are strongly influenced by both the Cu annealing and graphene growth steps as they determine

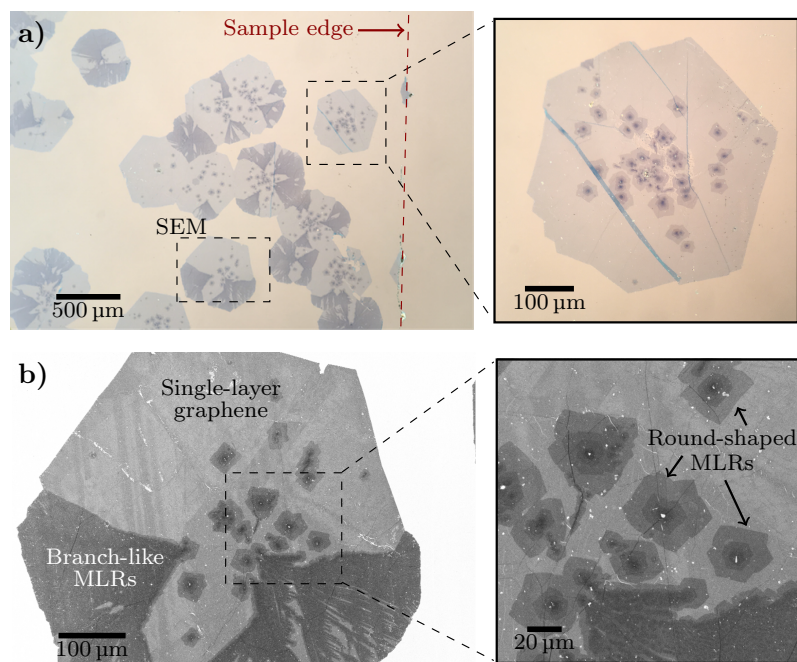


Figure 7.11: Graphene domains obtained after 1-hour long Cu annealing (Fig. 7.1,7.2: NAP, Ar/ O_2) and transferred on a SiO_2/Si substrate: a) Optical microscope images taken in the vicinity of the sample edge in order to observe compact and branch-like graphene MLRs. b) Scanning electron microscopy (SEM) images taken in the dashed rectangle displayed in a).

the graphene coverage rate and the C-based species adsorption at the Cu foil backside. Producing graphene with a relatively high nucleation site density promotes the rapid complete coverage of the Cu foil backside which acts as a passivation layer and suppresses the formation of these extra layers on the topside, even in the vicinity of the Cu substrate edge. Moreover, annealing the Cu foils at high temperature (1050°C) under a reducing atmosphere for a prolonged duration after annealing them in an oxygen containing atmosphere does not reduce the formation of these round-shaped MLRs but rather tends to increase their lateral size and

thickness. It is thus believed that the formation of these MLRs is not promoted via an O₂-activation process of the Cu surface as proposed by Hao et al. [206].

7.3.2 Branch-like multi-layer regions

The second kind of MLRs, which looks like branches growing radially along with the first layer, has exclusively been observed when the Cu annealing step has been performed under a hydrogen-free atmosphere and is randomly distributed over the entire Cu sample. This kind of MLR which, to our knowledge, has not been observed yet, exhibits some specific features (see optical images in Figs. 7.9-7.13). First, they seem to be randomly present underneath certain domains and completely absent in others. Second, it is observed that these branch-like MLRs are exclusively present underneath the compact domains and do not grow by themselves which suggests that the presence of a top first continuous and compact domain is necessary for their formation. Figures 7.11, 7.12 and 7.13 also show that the branches do not propagate beyond the top first layer domain edges which indicates that the presence of the first layer is necessary for the branches lateral growth. Furthermore, it seems that the growth of these branch-like underlayers stop growing when the top layer domain merges with another adjacent domain, which indicates that the branch-like MLRs formation relies on the methane reaction onto the Cu top surface in the vicinity of the domain and the surface diffusion of active C species underneath the top graphene layer. Finally, it is found that Cu grain orientation of the polycrystalline foil has rather little or no effect on the presence/formation of branch-like MLRs. Indeed, the presence of branch-like multilayer regions (see right panel in Fig. 7.12) does not seem to really match with the presence of certain underlying Cu grains (see left panel in Fig. 7.12).

The formation of branch-like MLRs might result from the Cu oxide layer present on top of the catalytic substrate that serves as a getter material and cause an accumulation of impurities in the vicinity of the Cu foil surface. Impurities such as residual metals might thus migrate towards



Figure 7.12: Optical microscope images taken before (left panel) and after the transfer process (right panel). Left panel shows the Cu surface underlying the graphene domains while the right panel shows the graphene additional layers.

the catalyst surface and get trapped in the surface oxide layer during the furnace warming and Cu annealing steps and subsequently possibly modify the graphene growth kinetics through a modification of the Cu surface catalytic activity and carbon solubility in the vicinity of the surface.

7.3.3 Characterization of millimeter-size GDs

Raman spectroscopy has been employed to evaluate the structural quality, the number of layers and the uniformity of the graphene films that have been produced. The Raman analysis has been conducted after transferring graphene onto thermal 300-nm-thick SiO₂/Si substrates. The dominant characteristics found in the Raman spectra are the D peak ($\sim 1350\text{ cm}^{-1}$), the G peak ($\sim 1580\text{ cm}^{-1}$) and the 2D peak ($\sim 2690\text{ cm}^{-1}$). Two Raman maps have been acquired in two different locations: one in the center of the graphene domain with a branch-like MLR and one at the junction between the multi-layer domain and the adjacent single-layer domain (as shown with dashed rotated rectangles in Fig. 7.13).

Both maps displayed in the middle and bottom panel of Fig. 7.13 exhibit a very low D peak-to-G peak intensity ratio which indicates that the disorder-induced D peak is very weak. Such small I_D/I_G ratios prove that the graphene sample is almost defect-free besides the presence of cracks that have been introduced during the transfer process and that are visible on the optical images [155,166]. It appears that the PMMA-assisted transfer process tends to produce more cracks in the graphene domains when a branch-like MLR is present underneath. This result is probably caused by the non-uniform graphene film rigidity and the presence of a mechanical stress gradient within the graphene domain film when the Cu foil is etched away. When analyzing the 2D peak-to-G peak intensity ratio of both maps, it can be observed that the regions that appear brighter on the optical images feature a I_{2D}/I_G ratio ranging from 1.8 to 3 which substantiates that these regions are single layer graphene.

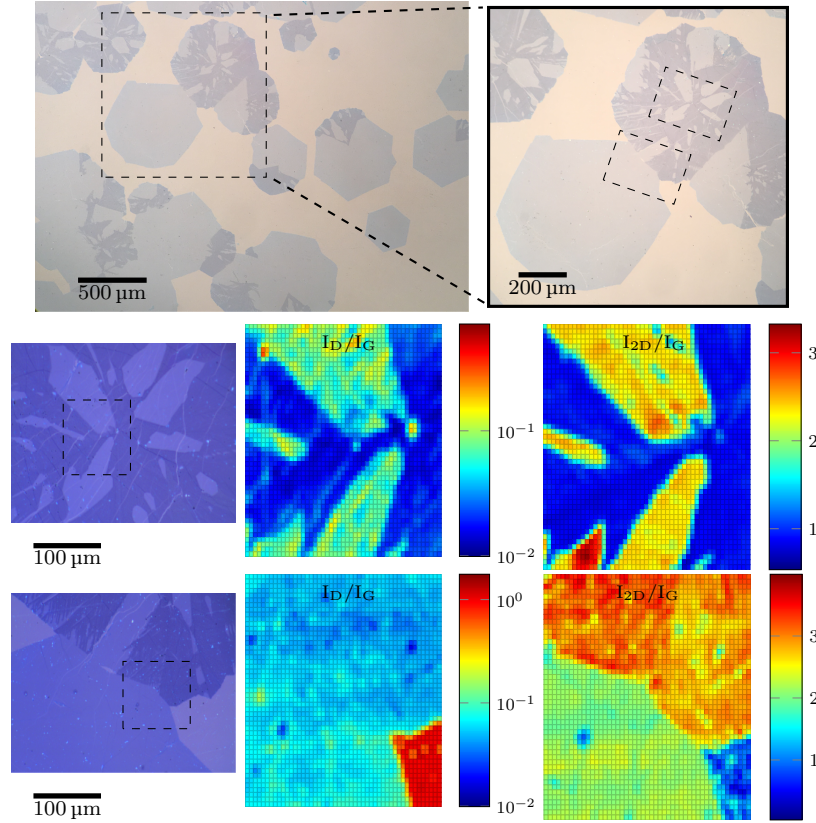


Figure 7.13: Raman spectroscopy analysis of graphene single- and multi-layer regions. First panel: Optical microscope image of graphene domains as-transferred on SiO_2/Si substrates. Second and third panel: higher magnification optical microscopy images of the dashed rotated squares in the first panel and corresponding Raman maps (50×50 data acquisitions over surface areas of $100 \mu\text{m} \times 100 \mu\text{m}$) of I_D/I_G and I_{2D}/I_G ratios.

Raman measurements performed in the multi-layer branch at the center of the graphene domain (see the middle panel of Fig. 7.13) exhibit a I_{2D}/I_G ratio of about 1 which is consistent with the Raman measurements of CVD-grown bi-, tri- or few-layer graphene widely reported in

the literature [75, 85, 164, 207, 208]. In contrast, the I_{2D}/I_G ratio corresponding to the multi-layer branch merging with the adjacent single-layer domain (see bottom panel of Fig. 7.13) is comprised in the 2.2-3.9 range. This rather unexpected result has also been obtained in other regions as shown in Ref. [116]. Regardless of whether the I_{2D}/I_G ratio is close to 1 or superior to 2, Raman spectra acquired in the multi-layer regions always exhibit a symmetrical 2D peak that can be fitted by a single Lorentzian function which is indicative of a turbostratic graphene multi-layer stack [164].

Figure 7.14 shows that the Raman spectra acquired in the multi-layer region of the bottom panel of Fig. 7.13 have a 2D peak which is narrower (FWHM_{2D} in the 22-30 cm^{-1} range) and has a slightly blueshifted position (2675-2690 cm^{-1}) compared with those acquired in single layer graphene regions which present a FWHM_{2D} in the 30-40 cm^{-1} range and a position in the 2665-2675 cm^{-1} range. On the other hand, the MLRs exhibiting a more conventional behavior, that is with a $I_{2D}/I_G \sim 1$, have wider 2D peaks ($\text{FWHM} \sim 40\text{-}60 \text{ cm}^{-1}$) which are further blueshifted (2690-2705 cm^{-1}). In order to observe the spatial variation of the position and full width at half maximum of the 2D band for different kind of multilayer regions, Raman mappings have been acquired and discussed (see Ref. [116]). These two Raman behaviors seem to differ from one multi-layer branch to another, even within a single graphene domain and are believed to be caused by a different relative rotation angle between the top layer (i.e. the millimeter-size domain) and the underlying additional layers. This explanation is consistent with previous work that showed a correlation between the I_{2D}/I_G ratio and the twisting angle in compact bi- and tri-layer graphene films [160–163].

Since Raman spectroscopy does not seem to be helpful in determining the thickness of the branch-like underlayer, atomic force microscopy (AFM) has been employed. Given that the PMMA-assisted transfer process of graphene does not reliably deposit graphene in close contact with the underlying SiO_2/Si substrates and often leaves traces of PMMA on graphene domain edges, the evaluation of the thickness has been

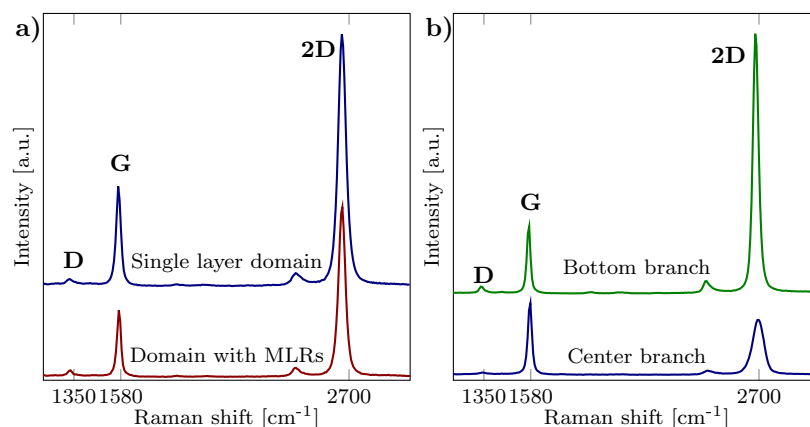


Figure 7.14: Typical Raman spectra acquired in (a) single layer regions from the single layer domain (top blue curve) and from the domain containing MLRs (bottom red curve) in Fig. 7.13, (b) MLRs from the bottom branch (top green curve) and from the center branch (bottom blue curve).

achieved by scanning the surface topography across graphene cracks. Figures 7.15a and 7.15b show PeakForce tapping-mode AFM images that have been acquired in single and multi-layer graphene regions respectively. The cracks appear as darker stripes with a width of a few hundreds of nanometers and are usually propagating perpendicularly to the wrinkles (narrow white lines).

In Fig. 7.15a, the crack spreads through the single-layer and reach the SiO₂ surface which appears rougher than the graphene film. By measuring the crack depth at various locations, the crack depth is evaluated to about 1.3 nm on average which is pretty thick but consistent with previous reports (see chapter 3). When performing similar depth measurements across cracks that propagated through a multi-layer stack (not shown here), the perceived depth lies around 2.2 nm. The difference in the crack depth measured in a single-layer and in a branch-like corresponds to about 2 times the theoretical distance between adjacent graphene planes. In order to corroborate these results, AFM measure-

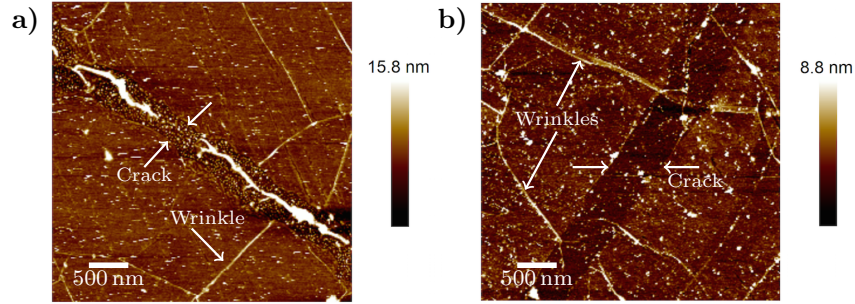


Figure 7.15: *PeakForce tapping-mode AFM topography images of graphene transferred on a SiO₂/Si substrate. a) Crack spreading through a single-layer graphene film. b) Crack partially spreading through a graphene branch-like MLR.*

ments have been carried out across a crack in a MLR which did not spread through the entire multi-layer graphene film as the cracked area contains wrinkles and a better surface roughness than the SiO₂ surface (see Figure 7.15b). The height difference between the crack area and the rest of the image is about 0.7-0.8 nm, hence supporting the assumption that the branch-like multi-layer regions contain 2 layers in addition to the single-crystalline graphene domain present on top.

7.4 Conclusions

In conclusion, we undertook a systematic study of the impact of the *in-situ* Cu annealing conditions on the subsequent growth of graphene. Our results show that the nucleation site density can be tuned over 4 orders of magnitude by adjusting the gas composition, global pressure level and Cu foil exposure time to high temperature.

The carbon concentration present on the Cu surface and dissolved in the Cu foil bulk prior to graphene growth appears to be the main factor governing the nucleation site density of graphene.

Introducing oxygen inside the CVD furnace, even trace amounts, is more effective to decrease the catalyst carbon content than using a reducing atmosphere and, therefore constitutes a key process condition for successfully producing graphene domains with lateral size exceeding a few millimeters. Our experiments provide a better understanding of the mechanisms that control the nucleation density and enrich the debate about the actual role of oxygen.

Finally, we found that using a hydrogen-free atmosphere prior to graphene growth can result in the formation of a new kind of defect-free multi-layer graphene that can extend over a few millimeters.

The improved understanding of the correlations between the Cu annealing conditions and the growth behavior provides clear guidelines for the synthesis of high-quality graphene films with a controllable number of layers.

Chapter 8

Conclusions and perspectives

Thesis conclusions

This thesis mainly focused on 4 key strategic axis:

1. The study of the synthesis platform which consists of either a Cu foil or a thin Cu film pre-deposited on a 3-inch substrate
2. The CVD setup design which has been modified over time in order to explore a wider range of CVD parameters and eventually reach more appropriate CVD conditions
3. The extensive investigation of the correlation between the CVD protocol and the obtained graphene growth results
4. The improvement of the transfer procedure which enables the deposition of graphene on other substrates that are more convenient for characterizing graphene or fabricating technological applications

These aspects contributed to a main goal: producing graphene with minimal crystalline defects and a controllable number of layers and facilitating its integration in advanced technological applications.

The major innovation of this thesis lies in the implementation of the pressure-controlled CVD equipment which is a versatile tool for carefully studying the impact of CVD parameters on the formation of graphene and addressing some issues related to the synthesis substrate. This customized CVD equipment lead to a series of novel and original findings:

- The realization of innovative CVD experiments which provide a deeper understanding of graphene growth mechanisms. In particular, the pressure-controlled CVD equipment is of great interest for decoupling the impact of the CVD parameters used during the Cu annealing and graphene growth steps on graphene formation. The exploration of a wide range of CVD parameters results in a series of new observations (i) demonstrating the argon-induced in-situ oxidation of Cu during the annealing step, (ii) shedding some light on the actual role of oxygen on the nucleation site density, (iii) and providing an insightful comparison between performing the graphene synthesis process under ambient pressure (APCVD) and low pressure (LPCVD) conditions.
- The use of a thin Cu film instead of a conventional Cu foil as catalyst for graphene growth. Graphene produced on a smooth, flat and rigid synthesis substrate is less likely to contain wrinkles once transferred on a device-compatible substrate or can be directly processed by conventional thin film technologies. Moreover, Cu films constitute an ideal synthesis substrate to rigorously study the growth of graphene owing to its high purity, its improved surface roughness and its geometry enabling the catalysis on one single surface. This last element is particularly important given that, in the case of Cu foils, it has been demonstrated that active C species generated at the Cu substrate backside can significantly contribute to the growth of graphene on the topside and form undesired multilayer regions.
- The discovery of a simple method to address the Cu film degradation issues upon the graphene production process. Our results show that performing a Cu annealing step under a high pressure

of Ar favors the growth of large domains but adversely impacts the Cu film physical integrity. The Cu film degradation, attributed to hydrogen embrittlement, can be avoided by evacuating the furnace for a brief moment prior to the graphene growth step.

- The excellent graphene synthesis results in terms of uniformity, scalability, thickness and structural quality. Single-layer graphene films with domains exceeding 1 mm have been produced on thin Cu films, which is the largest domain size reported to date on this kind of substrate. The good spatial uniformity obtained over large surface areas (3-inch wafers) paves the path for the large-scale integration of graphene in practical applications. Chapter 7 demonstrates a simple and efficient method to decrease the nucleation site density of graphene by about four orders of magnitude and successfully produce compact single-crystalline domains with a lateral dimension exceeding 2 mm on Cu foils, which is not a standard yet.
- The production of a new growth mode for the formation of defect-free multi-layer graphene that extends over distances exceeding 1 mm and exhibit peculiar Raman signatures. To our knowledge, this result is entirely novel and opens up several interesting scientific questions and possible practical applications. Along with these new branch-like multi-layer graphene regions, more conventional compact multi-layer graphene stacks have also been observed. The fundamental underlying mechanism for the formation of these additional layers is unraveled and a simple method is proposed to control or suppress their formation.

In conclusion, this thesis has enabled the implementation of the graphene CVD technology with state-of-the-art capabilities in the WINFAB research facility. As the lateral size of graphene domains is now commonly used as a metric for the structural quality, particular efforts have been directed to produce single-layer graphene made of millimeter-size single-crystalline domains. Our results offer a series of guidelines to control the synthesis protocol and produce graphene films with desired structural quality and number of layers. The insights gained from the development of the CVD synthesis equipment and protocols provide a framework to drive the manufacturing of graphene at the industrial-scale and can potentially facilitate the research and development for the CVD synthesis of other emergent 2D materials such as h-BN and MoS₂.

Perspectives

As aforementioned, the foremost challenge for the integration of graphene in technological applications lies in the development of manufacturing and processing techniques that satisfy the industrial demand for high performance, high reliability, high throughput and low cost. In this context, the better understanding of the complex graphene growth mechanisms, the various innovations and the novel observations provided in this thesis open up new research directions and offer some exciting perspectives:

1. Mass production of graphene:

Context: The chemical vapor deposition of graphene is a rather scalable technique as the produced graphene surface area is directly proportional to the catalyst surface area exposed to the CVD conditions. In this respect, recent technological advances have been made in improving the CVD production throughput. The continuous manufacturing of graphene has been demonstrated using a roll-to-roll processing method [209–212]. Batch CVD processing demonstrated the production of graphene sheets with dimensions up to 30 inches by rolling the Cu foil inside a 8× 39 inches CVD furnace or the production of 280 cm² of graphene by assembling twenty Cu foils (2×7 cm²) in a close-packed stack [181, 213]. However, inhomogeneous growth issues have been observed and attributed to temperature gradient inside the furnace or to the limited mean free path of reactive gases at the interface between adjacent Cu surfaces.

Challenges: Although these production approaches demonstrated advanced results in terms of throughput and production costs, they fall short when it comes to producing single-layer graphene with a high structural quality. As mentioned in chapter 7, the Cu foils require a relatively long-duration annealing at high temperature in order to achieve a low density of nucleation sites. It seems pretty challenging to incorporate such a step in the continuous manufacturing process of graphene. Batch

processing seems to be more convenient to perform a Cu annealing step prior to the graphene growth. However, the processed Cu surface area drastically depends on the CVD setup volume and configuration. From chapters 4 and 7, it seems evident that folding or rolling the Cu foils in order to fit a greater surface into a given CVD furnace volume does not represent a viable route as the long-duration high-temperature annealing will cause the Cu foil structure to soften, collapse and weld/stick together. Moreover, the high affinity of the Cu foil for oxygen will create a gradient of oxygen partial pressure along the gas flow mainstream path in the CVD atmosphere. In other words, the part of the Cu foil located close to the gas inlet will undergo severe oxidation while the one located nearby the gas exhaust will be exposed to an atmosphere depleted from oxygen. Similarly, the carbon precursors are going to be progressively consumed as they flow through the CVD furnace along the Cu surface, leading to its impoverishment in the atmosphere nearby the gas outlet. As a consequence, the graphene growth will not be uniform over the entire Cu sample. It is also important to avoid any gas flow blockade or congestion induced by the Cu foil structure in order to prevent localized Cu surface confinement effects.

Moreover, it is worth mentioning that folding Cu foils into specific structures optimizing the surface-to-volume ratio has a detrimental impact on graphene physical integrity as unfolding the structure results in localized strain which is very likely to introduce cracks in graphene.

Furthermore, chapter 7 demonstrated that the low density of nuclei required for the growth of large graphene domains results in a slow coverage rate of the Cu foil during the graphene growth step. Maintaining Cu surface uncovered by graphene for a longer duration favors the production of undesirable bi- and few-layer graphene regions underneath millimeter-size graphene domains on both sides of the Cu foil via the diffusion of active C species through the Cu foil thickness. Consequently, it is believed that optimizing the Cu surface area within a given CVD reactor space while simultaneously aiming at producing a high quality predominantly single-layer graphene film is challenging.

Solution: Using Cu films pre-deposited on flat, rigid and smooth substrates represents a more appealing approach to increase the production throughput while yielding a high quality and mainly single layer graphene. Cu films can be easily stacked or arranged vertically in a horizontal hot-wall furnace so that each Cu wafer is oriented in the same way relative to the gas flow mainstream. The high softening point of quartz or sapphire substrates ensures that the wafer will stand still during the high temperature process. As a consequence, the Cu film inter-distance can be adapted so that the graphene growth can be uniform over the Cu film wafer. Using a thin Cu film as catalyst also offers better results in terms of controllability over the number of layers as only one single surface catalyzes the adsorption of methane. Moreover, given the relatively high surface-to-volume ratio of Cu achieved with the thin film, the adsorption of methane by the Cu film bulk will be reduced by a factor of about 50 compared to thick Cu foils. Therefore, the local variation of methane concentration in the atmosphere along the gas flow mainstream will be less pronounced and less methane will be required to produce graphene. Finally, the higher purity and quasi-2D nature of the thin Cu films make them more sensitive to the presence of oxygen during the Cu annealing step and can be "decarbonized" more efficiently.

2. Further understanding the graphene growth mechanisms

Context: As explained in chapter 4, the actual impact of the Cu surface confinement on the graphene nuclei density, the growth rate or the growth front morphology is not well understood yet. The results presented in chapters 6 and 7 suggest that the undesired catalysis of carbonaceous vapors on Cu substrate prior to the graphene growth is one of the key factors dictating the nucleation site density. It is very likely that the Cu surface confinement contributes to reduce this undesired adsorption of active C species prior to graphene growth. To our knowledge, this aspect has not been addressed in the literature yet.

Challenges: There are several difficulties to address in order to rigorously study the impact of the Cu surface confinement. First, it is

essential to make sure that the observed graphene growth is the result of the diffusion of C precursors along the confined surface/interface and does not arise from the carbon content of the Cu foil bulk or from the diffusion of active C species through the Cu foil thickness after the adsorption of C precursors on the non-confined Cu surface. It is also crucial to realize that the Cu surface confinement also provides, to some extent, a gas blockade effect during the Cu annealing step which would, for instance, prevent the diffusion of oxygen along the interface. It is thus challenging to decouple the effect of the Cu annealing step on the graphene growth as this impact will have a variable effect over the Cu surface. Finally, the employed pressure regime plays a critical role as it controls both the diffusivity of gas species at the interface and the Cu evaporation rate.

Solution: The best way to unravel the various the Cu surface confinement impacts on graphene growth lies in precisely controlling (i) the origin of the carbon source contributing to the formation of graphene, (ii) the extent of Cu surface confinement over large surface areas, (iii) the pressure regime and, (iv) the Cu annealing conditions. These strict requirements can be satisfied by using the pressure-controlled CVD system which can precisely adjust the global pressure and the partial pressure of the various species of interest (H_2 , CH_4 , Ar, O_2) in conjunction with a flat, rigid and smooth catalyst with one single reactive surface.

3. Graphene transfer

Context: Recently, a few research groups demonstrated that the dry mechanical delamination of CVD graphene from its synthesis substrate is very promising for device fabrication purposes [169,196,214]. Circumventing the wet Cu etching or electrochemical delamination prevents the contact of graphene with Cu etchant and rinsing solutions, thus avoiding the contamination by Cu etchant residuals, Cu particles or even simply adsorbed water molecules. It is also more attractive for the fabrication of high-performance devices to use h-BN as supporting material (and

also as final substrate) as graphene does not contact any polymer or solvent during the transfer process step [215–218].

Challenge: Although the h-BN-assisted mechanical delamination technique provides amazing results in terms of electronic mobilities, it is more adapted to fundamental research rather than industrial processing of graphene. This mainly arises from the fact that (i) exfoliated h-BN flakes feature a relatively small size, (ii) the alignment of h-BN flakes with single-crystalline graphene domains is a cumbersome process, (iii) the successful delamination of graphene from its synthesis is not a highly reliable process.

Solution: The successful delamination of graphene as-grown on Cu requires the proper adhesion between the graphene and the h-BN flake. As this adhesion takes place through van der Waals forces, it is essential to achieve a proper contact between h-BN and graphene and also make sure that graphene does not adhere too much to the underlying Cu surface. The reduction of the adhesion force between graphene and Cu has been achieved through a slight natural (or intentional) oxidation of Cu the surface upon exposure to ambient atmosphere (or water vapor) at room (or higher) temperature [169, 196, 216, 219]. It has also been demonstrated that the adhesion of graphene on the underlying Cu and the Cu surface oxidation rate underneath graphene strongly depend on the Cu lattice orientation [171, 172, 220]. Producing graphene on an epitaxial thin Cu film seems to be very promising to facilitate the h-BN-assisted mechanical delamination technique for 3 reasons. First, performing the CVD process step using a Cu film evaporated on a C-plane sapphire substrate results in a ultra smooth Cu-grain-boundary-free Cu surface and an ultra flat graphene film. A better surface planarity contributes to improve the contact between graphene and the h-BN flake and thus to increase their cohesion. The absence of Cu grain boundary groove also reduces the chances of having the graphene film pinned down to the Cu surface. Second, the substrate on which the Cu film is deposited can be selected so that the as-grown epitaxial film exhibits an optimal texture for the mechanical delamination of graphene. Finally, the growth

of graphene achieved on epitaxial Cu film seems to exhibit a greatly improved physical integrity as the cracks and wrinkles are very difficult to see with the SEM or using the optical microscope after a Cu oxidation step (see Fig. 8.1).

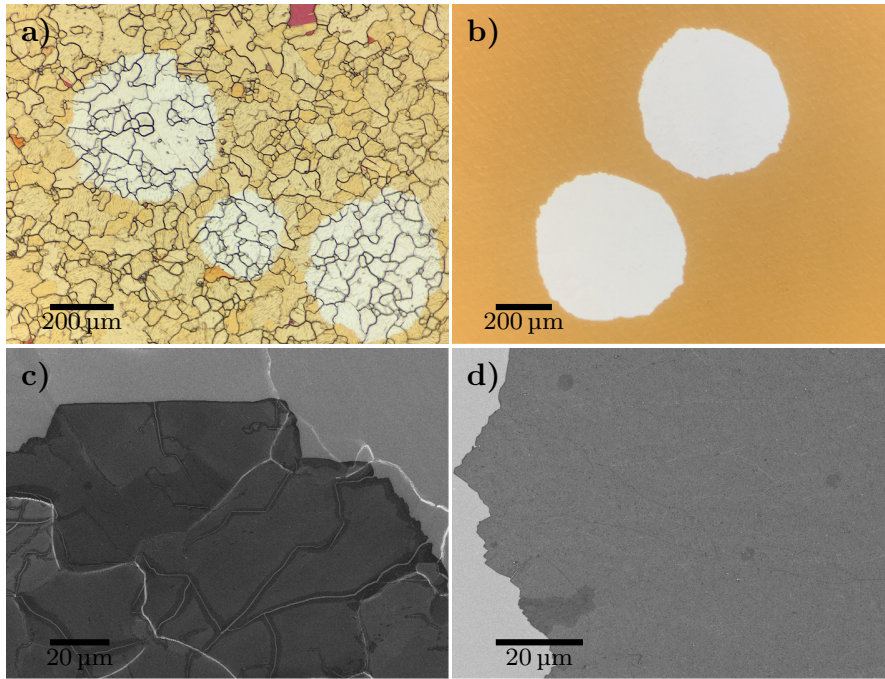


Figure 8.1: (a-b) Optical microscope and (c,d) in-lens SEM images of graphene as grown on Cu film pre-deposited on (a,c) a fused quartz and (b,d) a sapphire wafer.

4. Device fabrication

Defect-free graphene exhibits intrinsic remarkable electronic properties [2, 221]. However, many different mechanisms can cause the charge carriers scattering including (i) charged impurities deposited on top of graphene, trapped at the interface or present in the underlying substrate [2, 222], (ii) corrugations in the graphene sheet [223, 224], (iii) phonons in graphene or remote interfacial phonons in the substrate [225, 226], (iv) the formation of electron-hole puddles [227, 228] or even strain [229]. In order to prevent the deterioration of graphene performance induced by extrinsic scattering sources, graphene devices have been fabricated using suspended graphene or graphene encapsulated in h-BN.

Twisted multilayer graphene: Chapter 7 showed the production of multilayer graphene stacks with a high relative rotation angle and lateral dimensions exceeding several hundreds of micrometers. Intuitively, the synthesized electronically decoupled tri-layer graphene sheets could exhibit improved electronic properties compared with three single-layer graphene sheets. The bottom layer in contact with the underlying substrate can act as an intermediate substrate that mitigates the detrimental of the phonons and trapped charged impurities from the substrate and provides a smoother substrate for the upper layers. In a similar way, only the top layer is directly exposed to the atmosphere or transfer process-induced residues. It would thus be interesting to perform transport measurements in CVD-grown decoupled multilayer graphene.

On-ship suspended graphene structures: Growing graphene on epitaxial Cu films offers a relatively flat almost wrinkle- and defect-free graphene sheet on a rigid conducting substrate. The flat, rigid, smooth substrate can be directly processed by conventional CMOS technology techniques which can readily lead to the fabrication of graphene-based devices while circumventing the graphene transfer process step. The Cu film originally employed as a catalyst for the CVD process can thus be employed as a sacrificial layer to suspend graphene-based structures with

a relatively high yield. More complex architectures can also be designed in order to, for instance, probe the evolution of electronic transport in suspended graphene under mechanical tensile strain.

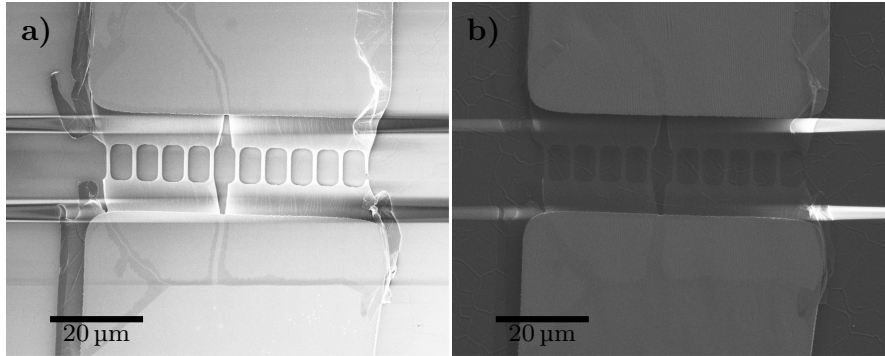


Figure 8.2: a) In-lens and b) E-T SEM images of a suspended graphene structure directly fabricated on the synthesis substrate by using the Cu film (pre-deposited on a fused quartz wafer) as a sacrificial layer. The yield of undamaged structures is relatively good provided that the graphene is crack free and the Cu film is grain-boundary-free.

Appendix **A**

List of references

Journal Publications

1. **B. Huet** and J.-P. Raskin. Pressure-controlled chemical vapor deposition of single-layer graphene with millimeter-size domains on thin copper film. *Chem. Mater.*, 29:3431 – 3440, 2017.
2. M. Hammad, J.-J. Adjizian, C.-H. Sacré, **B. Huet**, J.-C. Charlier, J.-P. Raskin, and T. Pardoen. Adhesionless and near-ideal contact behavior of graphene on Cu thin film. *Carbon*, 122:446 – 450, 2017.

Submitted Journal Publications

1. **B. Huet** and J.-P. Raskin. Role of Cu in-situ annealing in controlling the size and thickness of CVD graphene domains. To appear in *Carbon*, 2017.
2. M. Hammad, M. Fivel, **B. Huet**, C. D’haese, B. Nysten., J.-C. Charlier, J.-P. Raskin, and T. Pardoen. Single Layer Graphene Controlled Indentation Plasticity Mechanisms in Copper. Submitted to *Acta Materialia*.
3. M. Hammad, **B. Huet**, J.-P. Raskin, and T. Pardoen. Design, fabrication and development of on-chip tensile testing devices of suspended graphene beams. Submitted to *Microsystems & Nanoeengineering*

International conference contributions (talks)

1. **B. Huet**, J. C. Delgado, R. Vayrette, and J.-P. Raskin. Role of confinement in chemical vapor deposition of graphene on copper thin films. Material Research Society (MRS) Fall, Boston, United States, 2013.
2. **B. Huet**, M. Hammad, P.-A. Haddad, and J.-P. Raskin. Graphene growth, transfer and devices fabrication. 2015 NATO Advanced research workshop, Lviv, Ukraine, 2015.

International conference contributions (posters)

1. **B. Huet** and J.-P. Raskin. Low-Pressure CVD of Graphene On Thin Cu Film and Reliable Proximity Graphene Transfer For Electronic Applications. Cargèse International School, Frontier Research in Graphene Based Systems, Corsica, France, 2014.
2. **B. Huet**, M. Hammad, and J.-P. Raskin. Wafer-Scale Transfer of Graphene Grown on Thin Cu Film. Material Research Society (MRS) Fall, Boston, United States, 2014.
3. **B. Huet** and J.-P. Raskin. Growth of Spatially-Arranged Millimeter-Size Single-Crystal Graphene on Thin Cu Film. Material Research Society (MRS) Fall, Boston, United States, 2015.
4. **B. Huet** and J.-P. Raskin. Pressure-Controlled Chemical Vapor Deposition of Single-Layer Graphene with Millimeter-Size Domains on Thin Cu Film. Graphene2017, Barcelona, Spain, 2017.
5. **B. Huet** and J.-P. Raskin. Chemical Vapor Deposition Protocol Engineering for Controlling Graphene Single-Crystal Size and Thickness. Chem2DMat, Strasbourg, France, 2017.

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