CHEMICAL VAPOUR DEPOSITION (CVD) OF GRAPHENE ON TRANSITION METALS AND ITS PROTECTIVE PROPERTIES

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering

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SCHOOL OF PHYSICS AND ASTRONOMY
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II. Abstract

CHEMICAL VAPOUR DEPOSITION OF GRAPHENE ON TRANSITION METALS
AND ITS PROTECTIVE PROPERTIES

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The chemical vapour deposition (CVD) of graphene is the most promising route for the production of large-area high-quality graphene films. This work is devoted to the investigation of the CVD processes of graphene on transition metals, and to study the mechanisms of graphene growth on metals having different carbon solubility and, thus, different affinity to carbon.

In this work, three transition metals, copper, tantalum, and rhenium, were explored as growth substrates for graphene CVD. The last two metals are of interest for further investigation with the collaborators in the European Organization for Nuclear Research (CERN). The copper foil was chosen as a test metal since it is widely investigated object in the field of graphene production. Several growth factors have been modified to improve the graphene quality such as growth temperature, gas feeding ratio, and position of the substrate in the reaction tube. In addition to gas precursors used in this work, the formation of graphene from a liquid precursor of a biological origin was also studied.

The growth of graphene on tantalum was investigated using the isothermal-isobaric (at constant temperature and pressure) approach. The role of surface oxygen was found to be important for graphene formation on tantalum foil. In the case of rhenium, it was found that there is only a narrow window of growth temperatures for the deposition of graphene. Tantalum and rhenium are both refractory metals, but they have a drastically different affinity to carbon – low for tantalum and high for rhenium. Therefore, the mechanism of graphene formation on these two metals differs significantly.

In order to check the protective properties of deposited graphene, both metals were exposed to corrosive liquids and high-temperature oxidation. The obtained results confirmed the protective role of graphene and graphene-carbide surface layers.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AC</td>
<td>Amorphous carbon</td>
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<tr>
<td>APCVD</td>
<td>Atmospheric pressure chemical vapour deposition</td>
</tr>
<tr>
<td>BLG</td>
<td>Bilayer graphene</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FLG</td>
<td>Few-layer graphene</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>LPCVD</td>
<td>Low-pressure chemical vapour deposition</td>
</tr>
<tr>
<td>LL</td>
<td>Landau Level</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>ODFM</td>
<td>Optical dark field microscopy</td>
</tr>
<tr>
<td>SLG</td>
<td>Single layer graphene</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TM</td>
<td>Transition metal</td>
</tr>
<tr>
<td>TMDCs</td>
<td>transition metal dichalcogenides</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-high vacuum</td>
</tr>
<tr>
<td>vdw</td>
<td>van der Waals</td>
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</table>
1. **INTRODUCTION AND AIMS**

1.1 **MOTIVATION AND GOAL**

In the modern world, the development of medical treatments strongly relies on breakthroughs in science and technology. The application of radioisotopes in medicine was proposed shortly after the discovery of radioactivity about a century ago by Prof. Pierre Curie and MD. Henri Danlos\(^1\). Pure radioactive isotopes are often produced by proton irradiation of various targets including transition metals such as tantalum, rhenium, radioactive metals and their carbides.

About 50% of the 1.4 GeV CERN protons are sent onto targets to produce radioactive beams by online mass separation at the Isotope Separator Online Device (ISOLDE) facility, for a wide range of studies in fundamental and applied physics. CERN-MEDICIS is a spin-off dedicated to R&D in life sciences and medical applications. Target materials though lack stability and are often perform poorly in the air during the storage and transportation, and their surface has to be protected against corrosion\(^2\).

As graphene is chemically inert, owing to its impermeable for chemicals nature, it is an excellent candidate as a barrier material for application in anticorrosive coatings and can be used as corrosion protection for these metal targets. Furthermore, graphene can be grown conformally (preserving the correct angles between directions within small areas) on a piece of metal of any shape which makes it applicable to metal targets of any size, form, and dimension.

My project is a part of the MEDICIS-PROMED Innovative Training Network (ITN) under the Horizon 2020 EU program which aims at a primary scientific goal of providing and testing novel radioisotopes for nuclear medical imaging and radionuclide therapy. Within this project, I studied the potential and mechanisms of graphene growth on tantalum, rhenium and other metals to form a protective layer. This entailed the characterisation of the grown graphene layers and their ageing in a harsh environment.

The overall aim of this project is to develop corrosion-resistant protective coatings of radiological metal targets employing chemical vapour deposition of graphene. These targets are crucial in modern medicine, especially in the area of diagnostic imaging and radiotherapy, which is in concern in the overall MEDICIS-PROMED ITN project.
1.2 Types of Corrosion

The term corrosion originates from Latin *corrōdō* ("gnaw away"), is a general term for the spontaneous destruction of metals and alloys as a result of chemical, electrochemical or physicochemical interaction with the environment. In its common use, corrosion covers both oxidation of metals, microbial corrosion, galvanic corrosion, metal dusting, and pure chemical degradation.

There are generally two types of corrosion, including “dry” corrosion and “wet” corrosion. “Dry” corrosion is normally used for metal-gas or metal-vapour reactions, where oxidation of metals and reduction of non-metals take place at the same area. This form of corrosion is more commonly termed as “oxidation” of metals as direct chemical reactions between metals and environment are normally involved. On the other hand, in the case of “wet” corrosion, oxidation (or dissolution) of metals (anodic reaction) and reduction of non-metals (cathodic reaction) can occur at different places with corresponding electron transfer processes to complete electrochemical reactions. However, in this thesis, the focus is to discuss the dry and wet corrosion while leaving aside the influence of electrochemical corrosion.

There is a number of strategies for protecting surfaces. It includes the alloying with metals less susceptible to corrosion, sacrificial anodes, and barrier coatings. However, alloying by forming a stronger and more corrosion-resistant material can change the mechanical properties of the substrate. Anodic protection creates a galvanic system in which the substrate is less corroded metal and acts as a cathode, but it requires to replenish of a large bulk of the disposable metal. Surface coatings can be applied without any of these drawbacks; however, classical surface coatings do add to the thickness of the substrate, potentially ruining the tolerances of the item coated. Moreover, the interface between the coating and the substrate needs a strong adhesion, otherwise there is a risk of delamination.

Since this thesis is focused on the investigation of graphene as a protective layer, the third strategy will be explored. The ideal anticorrosion coating should meet the following requirements: (i) to be thin in order not to change the geometry of coated object, (ii) to be flexible and repeat the shape of substrate, (iii) to have a good adhesion to the substrate, (iv)
to be chemically stable/inert (do not dissolve or oxidise), (v) to be environmentally friendly and possibly to be inexpensive as well. One possible candidate today which comes close to fulfil all the requirements is graphene. However, graphene coatings are still in an early phase of development, and it has only been tested in stringent laboratory-based conditions. Nevertheless, in the work of Kravets et al., it was shown that copper films without graphene protection would not survive and, therefore, graphene-protected copper can be used in complex plasmonic devices that require nanofabrications. Also, protective properties can be demonstrated when applying graphene derivatives, as in work, where the exceptional barrier properties of multilayer graphitic films made of reduced graphene oxide were reported.

1.3 INTRODUCTION TO THE PROPERTIES OF GRAPHENE

1.3.1 Carbon allotropes

Carbon compounds make up 95% of all known chemical compounds, due to the tendency of carbon to combine with both electronegative and electropositive elements and moreover its ability to bond with itself in different configurations. The electronic configuration of carbon atoms in the ground state is 1s^22s^22p^2, making four electrons available to form covalent chemical bonds. Carbon tends to hybridise in one of the three known forms: sp, sp^2, or sp^3. The transition from the ground state, 1s^22s^22p^2, to the excited state, 1s^22s^12p^3, costs ≈ 4 eV to promote a 2s electron to the 2p, orbital state (Fig.1.1 and 1.2). However, bonding with other carbon atoms favours the formation of sp^3 hybridised orbitals, which lowers the total energy of the system (see Fig.1.1 rightmost panel for sp^2-hybridised state). Depending on the hybridisation type three main allotrope forms of carbon have been distinguished - diamond, graphite and amorphous carbon.

The variety in carbon hybridisation is reflected on the dimensionality of the formed molecules, and it, therefore, plays a significant part in establishing physical and chemical properties of carbon materials, i.e. sp^3 diamond is transparent, mechanically strong and an insulator. In contrast, sp^2 graphite comprising layers stacked on top of each other by weak van der Waals forces is grey, soft and electrically conductive. The most intriguing allotrope among them is graphite due to its electronic structure and similarity with ordinary metals.
1.3.2 Graphene: Definition and Structure

Graphene is one of the stacked layers of graphite organised in a two-dimensional honeycomb lattice. Despite the very close relation to graphite and other carbon-based
structures, graphene shows such a different behaviour, that it can be considered new material. The strong covalent bonds between carbon atoms in graphene result from atoms sharing one $s$ and two $p$ orbitals of the neighbouring atoms, to form an $sp^2$ bond with an interatomic distance of 1.42Å. In Fig. 1.3a, the two-dimensional hexagonal lattice structure of graphene is depicted with the unit cell vectors. The graphene cell comprises two interpenetrating triangular Bravais lattices, A and B, with one carbon atom per sublattice. The reciprocal lattice of a graphene crystal is also hexagonal with high symmetry. The graphene unit cell is a rhombus (the highlighted area in Fig. 1.3a) with two non-equivalent carbon atoms, A and B, which are represented by the blue and yellow circles.

![Graphene Crystal Structure](image)

Figure 1.3 The crystal structure of graphene, (a) 2D hexagonal lattice of graphene in real space with basis vectors $a_1$ and $a_2$ (the highlighted area represents the unit cell). (b) Brillouin Zone for graphene with the reciprocal lattice vectors $b_1$ and $b_2$. Adapted from\textsuperscript{11}.

Graphene exhibits significantly different electronic properties as compared to bulk graphite\textsuperscript{12}. A stack of 2-10 layers of graphene also exhibits intermediate properties that are different from a single sheet of graphene or a bulk graphite, which is defined as few-layer graphene (FLG)\textsuperscript{13}.

In Fig. 1.4 the most common stacking orientations for FLG obtained from exfoliation of natural graphite are shown\textsuperscript{14-16}. The most stable stacking order that can be seen in crystalline graphite such as highly oriented pyrolytic graphite (HOPG) and natural graphite is Bernal stacking (also called AB stacking) where half of the atoms lie directly over the centre of a hexagon in the lower graphene sheet, and half of the atoms lie over an atom or, less commonly, in the AA form, in which the layers are exactly aligned.
Figure 1.4. Common stacking orders found in multilayer graphene exfoliated from natural graphite. (a) hexagonal AA stacking, (b) Bernal AB Stacking, and. Shaded areas are unit cells. Images adapted from \(^\text{14}\).

Often in the case of a few layer graphene or graphite produced at low temperature, no stacking order can be observed. This type of random stacking is called turbostratic, where there are no preferential orientation angles between crystalline lattices of two adjacent graphene sheets.

1.3.3 **Electronic properties of graphene**

Many of the unique properties of graphene arise from its unusual crystal structure, the Brillouin zone of which is shown in Fig. 1.3b and Fig. 1.5. The two atoms in a monolayer graphene unit cell lead to the two ‘conical’ points per Brillouin Zone (BZ), which are close to the Fermi energy and lie at K and K' points where the valence and conduction bands meet. These points are also known as the charge neutrality or the Dirac points.
The dispersion relation of graphene near the Fermi level with a magnified view of the linear dispersion relation (Dirac cone). Images adapted from\textsuperscript{13}.

The absence of a band gap separating the valence and conduction bands and zero density of states at the Fermi level gives graphene its semimetallic character\textsuperscript{17}. Fig. 1.6 shows a comparison between the zero band gap structure in graphene and the standard band structure in semiconductors, highlighting the differences between the two. It should be noted that this density of states linearity does not exist in bi- or multilayer graphene.

It can be desirable to open a band gap in graphene, particularly for electronic and optical applications\textsuperscript{18}. There are various ways to achieve this, including mechanical, chemical and electrical methods (e.g. Fig. 1.7 shows band gap opening in bilayer graphene by applying perpendicular electric field). For example, a band gap was opened in monolayer graphene by applying a strain\textsuperscript{19} or by patterned adsorption of atomic hydrogen\textsuperscript{20}. A band gap can also be achieved by the deposition or adsorption of molecules on the graphene layer, e.g. water or ammonia\textsuperscript{21}. Through the use of numerical studies, various scholars have proven that the value of the energy gap can vary from few meV to hundreds of meV, depending on the methods used\textsuperscript{22}. 

Figure 1.5. The dispersion relation of graphene near the Fermi level with a magnified view of the linear dispersion relation (Dirac cone). Images adapted from\textsuperscript{13}.
The band structure of graphene changes when the number of layers increases, as in the case of bilayer or multilayer graphene. As an example, one of the simplest coupled layers can be found in Bernal stacked, bilayer graphene. The interlayer interactions lead to the formation of two pairs of parabolic bands instead of a single linear band at the Dirac point, Fig. 1.7.

![Bandgap Illustration](image)

Figure 1.7. Illustration of the bandgap in (a) monolayer and (b) bilayer graphene, showing zero band gap and (c) the effect of applying electrical fields (red arrows) in introducing asymmetry, yielding a bandgap that can be selectively tuned. Image adapted from.24.

### 1.3.4 Thermal properties

Most of the thermal properties of graphene are derived from those of graphite and bear the imprint of the highly anisotropic nature of this crystal. The specific heat of graphene is dominated by the lattice vibrational modes of the material (phonons) and is slightly higher than that of graphite and diamond below room temperature.25 The thermal properties of graphene and graphite at room temperature are dominated by the acoustic phonons.26 Initial measurements of thermal conductivity of graphene were conducted on suspended single-layer graphene with a value of 5300 W/mK or about 2000 - 4000 W/mK for freely
suspended samples\textsuperscript{27,28}. The value of the thermal conductivity of graphene is higher than those reported for carbon nanotubes\textsuperscript{29} or even for natural diamond\textsuperscript{30}. The presence of defects such as polymer residue from nanofabrication, edge roughness, polycrystalline grain boundaries, and disorder from contact with a substrate or a capping layer, indeed can degrade the thermal conductivity of graphene\textsuperscript{25}. Some studies propose the initial results on graphene’s ultrahigh thermal conductivity to be overestimated, however, a range between 1500–2500 W·m\textsuperscript{-1}·K\textsuperscript{-1} was still obtained\textsuperscript{31}, indicating that graphene is an excellent thermal conductor. Graphene’s superior thermal conductivity makes it an outstanding material for thermal management applications, such as condensation heat transfer systems\textsuperscript{32} and heat dissipators\textsuperscript{33}.

1.3.5 Impermeability

Bunch et al. tested the permeance of several gases through a micro-chamber capped with graphene sheet\textsuperscript{34}. It was experimentally demonstrated that graphene is impermeable to all gases, including helium at room temperature. Single layer graphene was placed on cavities etched into a silicon wafer; by changing the surrounding pressure, the graphene membranes acted as balloons due to the pressure difference. Furthermore, perfect single layer graphene is also impermeable to hydrogen atoms at ambient conditions, due to the high energy barrier for tunnelling through graphene’s dense electronic cloud\textsuperscript{35}. Also, it was demonstrated that no difference could be seen between using a single atomic layer of graphene and the maximum tested 75 atomic layers.\textsuperscript{34} However, a single missing atom defect lowers the potential barrier substantially (Fig. 1.8b).

Figure 1.8. (a) A graphene balloon that is impermeable to helium.\textsuperscript{34} (b) Density functional theory calculations showing aqueous proton transport through an atomic defect in graphene. Image adapted from.\textsuperscript{36}
Protons, for example, can also be transported through graphene in aqueous solution through atomic defects (Fig. 1.8b).

### 1.3.6 Protective (anticorrosive) properties

The unique impermeability and exceptional chemical inertness to corrosive species of graphene stem from the graphene crystal structure. As illustrated in Figure 1.9a, the size of the geometric pore is smaller than the van der Waals diameter of helium (0.140 nm), hydrogen (0.120 nm), oxygen (0.152 nm), sodium (0.227 nm) and chlorine (0.175 nm) etc. The significant energy barrier is required to overcome, for example, for oxygen atom (16.34 eV) to pass through the graphene lattice Figure 1.9b. Although the energy barrier can be lower when oxygen atoms take reaction paths, the energy barrier is still high enough to block the diffusion of oxygen through graphene lattice.

Figure 1.9. (a) Schematic illustration of the geometric pore of graphene lattice and (b) energy barrier for an oxygen atom to pass through graphene lattice from top to bottom with the fixed vertical path.

Permeability of graphene lattice was demonstrated only for protons (with energy lower than the 1.2–2.2 eV) with the clarification that this effect does not apply to double-layer graphene. The fact that proton transport through the graphene sheet does not meet obstacles should be taken into consideration when graphene is used as a corrosion barrier to protect metals in acidic media.

The proof of CVD graphene’s ability to protect against corrosion was reported by Chen et al. The work showed that a single sheet of graphene was able to protect a US penny from corrosion when immersed in 30% H₂O₂ for 2 minutes (Figure 1.10).
Report of Prasai et al. quantified the corrosion inhibition efficiency of CVD graphene coatings on Cu and Ni. It was shown that CVD graphene coatings on metal surfaces reduced the corrosion rates of Cu and Ni by 7 and 20 times, respectively. When CVD graphene layers are transferred to the surface, Kirkland et al. explained that the reduction of corrosion rate for CVD graphene coated Ni and Cu are primarily due to anodic-cathodic processes - dissolution process for Ni and oxygen reduction reactions for Cu. There are some factors, however, which significantly limit the application of CVD graphene for anticorrosive coatings.

Figure 1.10 (a) Schematic illustration on CVD graphene as a noble physical barrier and (b) an image showing graphene covered (upper) and uncovered (lower) US penny after immersion in H$_2$O$_2$ for 2 minutes. Images adapted from.

The CVD grown graphene often is far from its ideal properties containing many defects. Thus, cracks, wrinkles and grain boundaries in graphene deposited sheet can induce the corrosion. According to results reported by Schriver et al. and Zhou et al., corrosion of graphene coated Cu is accelerated at long-term exposure in air. Perhaps the deposition of the materials to passivate the defects can also increase the corrosion inhibition efficiency; however, these methods increase the cost of graphene coatings and greatly decrease their potential for real applications. Owing to its high electrical conductivity and being in direct contact with the metal substrate, deposited graphene can accelerate the galvanic corrosion rate.

At graphene defects, electrons which Cu loses due to oxidation are transferred away because graphene is a more efficient conductive pathway than Cu and reacts with oxygen for cathodic reaction (Figure 1.11). In seawater, graphene on the surface will also serve as a cathode and increase the corrosion rate of Cu.
The next factor limiting the application of graphene as anticorrosive coatings is a weak adhesion of graphene on some metal substrates\textsuperscript{50,51}. When graphene covers the metal which interacts with carbon weakly (e.g. Cu or Pt) it can easily be decoupled from the surface upon air exposure, providing a pathway for the intercalation of oxidising species to the whole metal surface (Figure 1.12).

In case of strongly interacting metals (e.g., Ni, Co, Fe), oxygen is not able to diffuse at the interface, and the oxidising species are, thus, only able to access the metal surface close to graphene defects.

On metals that form a passivating oxide (e.g., Ni, Co), these regions beneath the defects are quickly “plugged” by oxide formation, providing continuous long-term protection. For metals whose oxides are porous and not passivating (e.g., Fe), oxidation is initially slowed by the already formed oxide, and thus long-term protection is not possible, and graphene coverage provides only short-term passivation\textsuperscript{52}.

The weak adhesion is also attributed to the transferred graphene from one substrate to another, as transferred graphene is reported to be easily delaminated from a metal substrate even under normal working conditions at short-term.

Figure 1.11. Schematic illustration of the corrosion mechanism of graphene coated Cu (G/Cu). Images adapted from.\textsuperscript{49}
In summary, although CVD graphene has the potential as a coating for corrosion protection of metals and alloys, graphene defects, galvanic coupling issues, weak adhesion to metallic substrates and the roughness of the metal surface need to be considered.

1.4 APPLICATIONS OF GRAPHENE

Graphene is already being used in electronics (prototype devices),\textsuperscript{54,55} energy storage,\textsuperscript{56} photonics,\textsuperscript{57} composite materials,\textsuperscript{58} sensors technology\textsuperscript{59}. Thanks to its conductivity, inertness and large surface area (high aspect ratio), graphene is ideal for composite materials. Graphene-based composites have been used as protective barriers against corrosion, fillers in carbon fibres, and strain reducing elements in polymers\textsuperscript{60}.

1.4.1 Field effect transistors

Graphene grown for high-speed electronic devices needs two important factors, high mobility of electrons/holes at room temperature and the presence of a band gap\textsuperscript{61}. The band gap is needed for switching the device on and off. The carrier mobility is perhaps the most important measure of the quality in graphene in the field of electrical device fabrication. Characterising carrier mobility in graphene is commonly done through graphene-based field effect transistors (GFETs).
A GFET device is characterised by applying a voltage between the source and the drain electrodes and measuring the current while changing the gate potential. The gate potential changes the carrier density in the device material (in this case, graphene). (Fig. 1.13) The change in resistance of the graphene as a function of back gate potential relates to the conductance of the graphene. Measurements of the electronic properties of graphene have shown electron mobilities of 40000 cm$^2$/V·s$^{-1}$ and high thermal conductivity of 600 Wm$^{-1}$K$^{-1}$, both much greater than typical semiconductors and metals, see Table 1.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electron mobility [cm$^2$/V·s]</th>
<th>Hole mobility [cm$^2$/V·s]</th>
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</thead>
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<tr>
<td>Si</td>
<td>1417</td>
<td>471$^{63}$</td>
</tr>
<tr>
<td>Ge</td>
<td>3900</td>
<td>1900$^{63}$</td>
</tr>
<tr>
<td>GaAs</td>
<td>8800</td>
<td>400$^{63}$</td>
</tr>
<tr>
<td>Graphene</td>
<td>100 000</td>
<td>100 000$^{64}$</td>
</tr>
<tr>
<td>CVD Graphene</td>
<td>450000</td>
<td>450000$^{65}$</td>
</tr>
</tbody>
</table>

Table 1.1 Comparison of carrier mobility measurements at room temperature for typical semiconductors and graphene.

It should be noted that the properties of graphene are very sensitive to its layer number, and all these excellent performances are true for a monolayer of graphene$^{66}$.

The application of CVD-grown graphene in FET will be presented below in the next chapters.
2. METHODS FOR GRAPHENE PRODUCTION

There are many methods of graphene production which recently have been developed depending on the application end, including (i) mechanical cleavage, (ii) liquid phase exfoliation, (iii) chemical reduction, (iv) epitaxial growth on SiC, and chemical vapour deposition (CVD). The main focus of this thesis is CVD graphene on different metal substrates, but a brief review of the number of graphene production methods would make a comprehensive comparison and highlight the advantages of the CVD process. Figure 2.1 summarises the main techniques used to produce graphene, which will be presented briefly in the following paragraphs.

![Graphene Fabrication Methods](image)

Figure 2.1. Graphene fabrication methods compared by quality vs value. Adapted from 73.

2.1 MECHANICAL EXFOLIATION

Since graphene sheets in graphite are held together by weak van der Waals forces, this allows layers to be easily peeled or slid off from each other. One of the earliest attempts to micromechanically exfoliate HOPG using AFM tip were exploited to peel off thin layers of graphite and laid down onto Si substrate. However, through these attempts, graphitic blocks were with thicknesses of above 10 nm. Figure 2.2 shows the SEM images of these micrographite structures.
Figure 2.2. One of the earliest attempts to mechanically exfoliate graphene from HOPG: (a) and (b) are SEM images of graphite layers peeled away by AFM tip\textsuperscript{74}. (c) and (d) are the images of transferred graphite onto SiO\textsubscript{2} substrates from a tipless AFM cantilever with which slabs of HOPG were deposited on, and an image of a typical device fabricated for electrical measurements\textsuperscript{75}.

The most common method now of separating the layers is the original Scotch tape method as used in graphene’s original isolation\textsuperscript{67,76}. This method utilises an adhesive tape to peel off graphene layers from HOPG. First, it comes several layers of bulk graphite, and, after repeatedly adhered to a fresh part of the tape, sheets of few layers to a single one, can be deposited.

The monolayers can be observed by optical microscopy (Fig. 2.3), and the thickness can be verified by Raman spectroscopy. This method, however, has the limitations. The areal dimensions of the largest measured monolayer flakes are no bigger than 1 mm,\textsuperscript{77} the position of the flakes are uncontrollable making device fabrication a product of luck and often no usable graphene is created. Despite the limitation on the size of the graphene flakes, mechanical cleavage is a very reproducible and reliable technique for the fabrication of high-quality graphene in research laboratories worldwide. It is also a low budget technique, and the quality of produced graphene is very high; however, controlling the produced graphene layer thickness is challenging, distribution of flakes on the substrate are random which makes this method is suitable for research but not for commercial production.
2.2 CHEMICAL EXFOLIATION

Liquid-phase (or chemical) exfoliation relies on using ultrasound, chemical, or electrochemical energy to exfoliate bulk graphite within a solvent which has a suitable surface tension to stabilise the resulting graphene. Synthesis of graphene by chemical exfoliation of graphite has three main routes: direct sonication of graphite in an organic solvent or surfactant solution, electrochemical exfoliation of graphite, and intercalation-exfoliation of graphite. The yield of these processes is typically a few percent; hence centrifugation is used to obtain a significant fraction of monolayer and few-layer graphene flakes in the final suspension.

2.3 GROWTH ON SILICON CARBIDE

Several graphene layers can also be obtained by thermal annealing of single crystal silicon carbide (SiC). The first epitaxial growth of such graphene layers was reported by Bommel et al. in 1975. Despite the attractive possibility to produce the graphene sheet on a large scale (of the size of SiC wafer), this method also has the drawbacks. The graphene formed by thermal decomposition of SiC is rotationally disordered, and the vertical roughness of the graphitic film is not uniform. Also, the cost of SiC substrates, the processing conditions at high temperatures (~1400 °C), and a very high vacuum (~10^-10 Torr) make this method very challenging. On the other hand, epitaxial graphene is by definition already on a dielectric substrate (SiC) and can thus be used directly for device manufacturing, which in some cases
is a great advantage. However, it also means the graphene layers cannot be transferred to an arbitrary substrate.

### 2.4 CHEMICAL VAPOUR DEPOSITION OF GRAPHENE

Chemical vapour deposition (CVD) of graphene on metal substrates is perhaps the most common large scale growth technique\textsuperscript{70} producing uniform samples with a higher yield of single layer areas than exfoliated graphene\textsuperscript{55}. CVD is defined as the deposition of a solid resulting from chemical reactions in gasses on hot surfaces\textsuperscript{85}. In CVD, the reactive gases are fed from cylinders into the reactor through a gas delivery system. The gas delivery system contains valves, mass flow controllers (MFCs), and the gas-mixing unit, which mixes the different gases according to their required ratios before they enter the reactor. The reactor (reaction chamber) is a place where the chemical reaction takes place and where the products are deposited on substrates. Heating elements surround the reaction chamber, thus providing the necessary temperatures for the reaction to occur. Finally, the by-products of the reaction and the non-reacted gases are removed by the gas delivery system through the exhaust\textsuperscript{86}. The first successful attempt to grow graphene using CVD was reported by Somani and his group in 2006 by using camphor as a carbon source, and Ni foil as the hot substrate\textsuperscript{87}. Even though the resulted graphene comprised many layers, this method showed the promise of the synthesis of monolayer graphene by CVD.

The breakthrough in this area was made in Ruoff’s group when reported the CVD of single-layer graphene on Cu substrate\textsuperscript{71}. A 25 μm thick Cu foil was annealed in a hydrogen atmosphere at 1000 °C, followed by introducing methane at low pressure. The resulting deposited graphitic film was ~95% SLG with a small percentage of FLG.

Many metals were later used to investigate the possibility of widening the window of CVD graphene substrates. Metals such as ruthenium (Ru),\textsuperscript{88} iridium (Ir),\textsuperscript{89} cobalt (Co),\textsuperscript{90} and palladium (Pd)\textsuperscript{91} were all used to grow graphene, in addition to Ni and Cu. Therefore, the CVD route can potentially meet the thin film applications demands for graphene, in terms of cost, quality and scalability.

A common CVD system set-up is a hot-walled tube furnace; the substrate is positioned within a heat resistant tube with a gas precursor flow; this is all heated within a furnace/oven facilitating the CVD process as shown in Figure 2.4. Cold-walled methods have also shown promise in which only the substrate is heated using a hot substrate platform/holder\textsuperscript{92}.
2.4.1 Mechanism of graphene formation

Even though graphene is remarkably easy to grow on metals, the atomic-scale growth mechanisms behind these processes are not straightforward. In general, the growth mechanism is strikingly different from that of a conventional heteroepitaxy. Epitaxy refers to a process of depositing a single crystalline film onto the surface of a single crystal substrate. If the deposited film is of the same substrate material, it is called a homo-epitaxial layer, and if it is different from the substrate materials (like graphene), it is called a hetero-epitaxial layer.

In the CVD process, the quality of formed graphene: thickness, stacking, and crystalline orientations of graphene layers obtained, primarily depends on the metal used. Metal-carbon interactions determine the mechanisms of growth and lead to different growth morphologies. The CVD of graphene is a catalytic process, with the transition metal substrates acting as a catalyst material. By definition, a catalyst accelerates reaction without itself being consumed in the reaction. The catalyst provides a low activation energy pathway to avoid slow reaction rates, compared with the uncatalysed reaction.

At elevated temperatures and pressures, carbon dissolves into the surface of the substrate during CVD, the amount of carbon that the substrate intakes is defined as its solubility. Metal that dissolves carbon at or near the growth temperature is favourable for FLG deposition. Thus, the carbon intake by metal is a critical parameter for choosing a catalyst for graphene growth. Generally, metals with partially filled d-orbitals have more interaction toward carbon than metals with completely filled d-orbitals.
Of the numerous types of suitable metals, Ni and Cu are the most promising for cost-effective and large area deposition. The mechanism of graphene growth is, however, different for these two metals (Fig. 2.5). In the case of Ni, which has partially filled d-orbitals, 1.3 wt% of carbon dissolves into the Ni substrate at 1000˚C. Nickel has been originally suggested for graphene synthesis and would have some advantages over copper if multilayer graphene formation could be avoided. In work\textsuperscript{96}, however, it has been demonstrated that the growth of graphene on Ni is not via segregation through the bulk upon cooling, but rather through surface growth mode and therefore a similar self-terminating monolayer growth as for copper was achieved. Although, the important fact was that graphene was grown by UHV CVD at pressure $10^{-6}$ Torr, which could significantly suppress the solubility of carbon into Ni.

The mechanism of graphene growth on Cu, which has no partially filled d-orbitals to interact with carbon, is different from Ni. Carbon cannot diffuse into the substrate at typical growth temperatures due to the negligible solubility of carbon in Cu ($<0.04$ wt% at 1000˚C). Therefore, graphene on Cu is formed by the direct decomposition of the hydrocarbon (CH\textsubscript{4}) gas and 2D crystallisation effects on the substrate surface. After nucleation of graphene, progressive covering of the surface continues until the catalytic decomposition of hydrocarbon stops (Fig. 2.6). The mechanism has been verified by using $^{12}$CH\textsubscript{4} and $^{13}$CH\textsubscript{4} carbon precursors and Raman mapping\textsuperscript{97}. 

\textbf{Figure 2.5.} Growth mechanisms of graphene by CVD on various catalysts: Case of CH\textsubscript{4} growth on Ni and Cu\textsuperscript{95}. 


Figure 2.6. SEM image of graphene grown on polycrystalline Cu for different growth times. A) 1 min, B) 2 min, C) 10 min, and D) 60 min. The graphene nuclei form at random sites on Cu (A), enlarge and emerge to form a continuous film of graphene (B-C). The growth self-terminates as Cu surface is entirely covered by the monolayer graphene (D). Image adapted from\textsuperscript{71}.

Thus, it is not surprising that metals such as copper are proving to be popular, low-cost substrates for graphene growth.

Many works from literature, however, report deposition of bi- or even multilayer graphene on Cu\textsuperscript{98} at a single nucleation centre in addition to a monolayer. This behaviour deviates from the self-limited picture of monolayer growth on Cu. Various mechanisms such as the release of carbon during cooling from defects sites,\textsuperscript{99} differences in gas flow conditions on surface defects sites that leads to a greater flux of carbon precursors toward surface protrusions\textsuperscript{100}, and vapour phase decomposition of hydrocarbons by Cu vapour\textsuperscript{101} have been proposed to explain the multilayer formation. It is worth noting that most of the proposed mechanisms of graphene growth on Cu in the literature so far are either too phenomenological or too narrow in terms of applicability and heavily relying on computational modelling and simulations under idealised conditions\textsuperscript{102-104}.

The most common substrates for the CVD growth are polycrystalline foils as they are cheaply available. However, polycrystalline foils exhibit grain boundaries which can nucleate extra layers and random surface facets of different crystal orientations resulting in nonuniformity\textsuperscript{105,106}. The different crystal facets are known to affect the growth behaviour and quality of the graphene overlayer\textsuperscript{107}. In addition, step edges produced by surface
roughness or vicinal surfaces can also result in different nucleation and growth behaviour from perfectly flat surfaces (Fig. 2.7).\textsuperscript{108,109} Thin metal films grown on single crystal substrates such as sapphire or MgO have been used to overcome this problem resulting in uniform single crystal substrate\textsuperscript{107}. Using liquid Cu at growth temperature above its melting point (> 1080°C) is another way to eliminate the Cu grain boundaries and obtain a uniform, high-quality graphene\textsuperscript{110}.

Figure 2.7. STM topography of graphene islands formed on Ir (111) step edges with different growth times and atomistic model of graphene island growth\textsuperscript{108,109}.

2.4.2 Influence of temperature and pressure

Temperature plays a vital role in the CVD growth of graphene since thermal energy supplies the energy required to decompose the carbon source and to prepare the substrate surface as well. Figure 2.8 presents the influence of temperature and time on the resulted continuous graphene film. The exact growth process of graphene on Cu is still debated\textsuperscript{111,112}, however, it is well known that low growth temperature (~ 600°C) led to a high nucleation density of graphene and poor graphene coverage on the Cu surface\textsuperscript{112}, whereas the increasing temperature has its limits because it can also lead to poor quality of graphene films. In work by Fan et al.\textsuperscript{113}, it was reported that growth at temperatures near the melting point of substrate resulted in the formation of holes in the graphene film. These holes are believed to be due to the evaporation of the copper damaging the depositing film\textsuperscript{113}. 
Figure 2.8. SEM images of graphene nuclei grown on Cu with respect to different growth temperatures and times. Image adapted from 9.

Growth pressure is also an important controlling parameter for the CVD of graphene. Growth at atmospheric pressure ensures a rapid diffusion rate of carbon species to the metal substrate, which makes the carbon surface precipitation difficult to control. Atmospheric pressure chemical vapour deposition (APCVD) tends to give a few-layer graphene\textsuperscript{114} or films with a high concentration of defects and few-layer regions\textsuperscript{100,115}. One study suggests that APCVD leads to a Bernal stacking order and low-pressure chemical vapour deposition (LPCVD) to turbostratically stacked graphene\textsuperscript{116}. Graphene growth on Cu under low pressure shows predominantly a monolayer of graphene since there is no supersaturation of carbon species on the copper surface\textsuperscript{117}. The supersaturation model gives the attachment of single carbon adatoms to a graphene edge as the rate-limiting step in the film growth so that as the temperature increases a greater proportion of the adsorbed carbon can surmount the energy barrier to attachment and participate in graphene formation\textsuperscript{118}. Moreover, the kinetics of deposition is changed with pressure, i.e. the rate-limiting step in atmospheric pressure will be the surface reaction, while in low pressure the diffusion of carbon species from the bulk to the metal surface is
the rate-limiting step. Furthermore, low pressure and high temperature normally contribute to sublimation of the metal, which leads to a lower nucleation density\textsuperscript{100,119}.

The mutual influence of temperature and pressure on resulted graphene formation are presented in Figure 2.9.

![Figure 2.9. The effect of growth parameters such as temperature (T), methane flow rate (J\textsubscript{Me}), and methane partial pressure (P\textsubscript{Me}) on the domain size of CVD-grown graphene. Figure from\textsuperscript{120}.](image)

**2.4.3 Effect of carbon precursor sources**

The type of carbon source is an important parameter because it mostly influences kinetics and yield. As some species need higher/lower temperatures and pressures for dissociation to atomic carbon, this will affect the rate of growth and the continuity of graphene also. Many sources of carbon such as camphor\textsuperscript{87} liquids (e.g. benzene\textsuperscript{121}, toluene\textsuperscript{122}, ethanol\textsuperscript{123}), polymers [e.g. polymethylmethacrylate (PMMA),\textsuperscript{124} polystyrene (PS),\textsuperscript{125}] and other organic materials\textsuperscript{126} have been investigated to produce graphene films of various thicknesses. The efficiency of these sources for graphene production has not yet been fully investigated. The most common source is CH\textsubscript{4}, which is known to be less reactive than acetylene, ethylene, and alcohols, but it makes the growth more controllable. Generally, a low feed rate of the carbon source is preferred for uniform monolayer graphene growth with high crystal quality\textsuperscript{120,127}. 
2.4.4 Effect of carrier gases and hydrogen

Inert gases (e.g. Ar and N₂) which are introduced into the system during the growth as carrier gasses are unlikely to be involved in the reactions, whereas H₂ plays an important role in cleaning the catalyst substrate during annealing step by etching away oxides, amorphous carbon that usually forms in excess of the carbon precursor. Atomic H creates sites that lead to the dehydrogenation of CH₄ (the reaction that involves the removal of hydrogen from an organic molecule) and the creation of carbon radicals on the substrate surface. This formation of active surface-bound CₓHₓ results in graphene growth. Consequently, hydrogen slows down the deposition kinetics of graphene on Cu surfaces by blocking surface sites and reduce their number for CH₄ chemisorption. Vlassiouk et al. reported difficulties in depositing graphene when hydrogen is not added to the methane feedstock during the growth stage. Moreover, hydrogen plays a role in limiting the graphene thickness by carbon etching as it removes the weak C-C bonds. Lee et al. reported that bilayer graphene is more likely to be grown when the partial pressure of hydrogen introduced to the reaction chamber is low. However, the too great H₂ flow rate may lead to desorption of reactants etching off the deposited film during its growth process.

Hydrogen seems to play an important role in the CVD of graphene, and its role is important even at heating (annealing) stage (Fig. 2.10). As the hydrogen etches the surface during the annealing process, it reduces the sites for graphene formation, i.e. it decreases the nucleation density.
Figure 2.10. Influence of hydrogen in the heating process on nucleation density. Left – without hydrogen, right – with hydrogen. Image adapted from\textsuperscript{133}.

It must be also noted that at high temperature and very low-pressure conditions in the absence or at a low flow rate of the carrier gas (e.g. UHV conditions), significant sublimation of the substrate metal can occur due to its finite vapour pressure during graphene growth affecting the growth morphology\textsuperscript{134}. Thus, further investigation of overall pressure and the role of carrier gases are also required.
3. CHARACTERISATION OF GRAPHENE

3.1 OPTICAL MICROSCOPY

Optical microscopy is a quick and straightforward method to observe both CVD graphene as grown on a metal substrate and transferred to another substrate (usually SiO$_2$/Si wafers). To simplify the observation of graphene on Cu the dark field mode of an optical microscope is often applied. The observation of graphene flakes via dark field mode was reported by A. Lewis et al.$^{135}$ Such dark field mode provides clear, high contrast image of graphene films grown on copper, Fig. 3.1a. Also, it indicates deposition morphology and helps to determine the regions that need further investigation.

CVD graphene specifically can be observed directly on the copper substrate on which it is deposited, by growing a partially covering layer of graphene. Regions of a copper surface with a graphene coating can be quickly identified by subjecting the sample to corrosive conditions,$^{136,137}$ for example, by placing the copper foil on a hot plate at 160°C for 5-6 minutes$^{138}$ under ambient atmosphere. The oxidation process of the copper will occur faster, where there is no graphene than where graphene is protecting the copper surface, giving rise to the contrast between oxidised an un-oxidised copper, as seen in Figure 3.1b.

Therefore, optical microscopy is a very simple technique useful for indicating whether a CVD run has been successful; however neither the number of graphene layers deposited nor the quality of the deposited layers are revealed.

Figure 3.1. Optical images of graphene flakes. (a) Dark field mode of an optical microscope. (b) Same flakes after oxidising on the hot plate (150 °C for 5 min).
Conventional reflection mode of optical imaging can be used to reveal the percentage of graphene coverage on the growth substrate. Duong et al. have demonstrated the use of optical microscopy to visualise graphene grain boundaries and distinguish them from the grain boundaries of the copper substrate by using robust oxidation of the substrate copper foil after ultraviolet exposure under ambient moisture conditions.

3.2 Raman Spectral Features of Graphene

Raman spectroscopy has a long history of being considered a powerful technique for the structural characterisation of graphitic materials. Raman spectroscopy is a form of molecular spectroscopy based on the Raman effect or Raman scattering. When light (photons) interacts with any material or matter, some of the photons may be absorbed, reflected, transmitted or scattered (Fig. 3.2a). Most of the scattered photons have the same frequency (and thus energy) as that of the incident beam, and this elastic process is called Rayleigh scattering (or elastic scattering), Fig. 3.2b. When incident light is inelastically scattered by a vibrational mode of a chemical bond, a Raman photon is emitted. This emitted Raman radiation is shifted in frequency from the excitation light since energy is exchanged with the material, resulting in peaks in the Raman spectrum, which correspond to phonon modes in the sample. In the measurements, laser sources in the visible, near infrared or ultraviolet light range are used.

Figure 3.2. The ways light interacts with a material (a), schematic representation of fluorescence, Rayleigh scattering, Stokes Raman scattering, Anti-Stokes Raman scattering (b). Image adapted from.

The identification of graphene and its derivatives via Raman spectroscopy relies on three main bands, D, G and 2D bands (the latter is also known as the G´ band), Fig. 3.3a. These
bands dominate the Raman spectrum due to the resonance between carbon sp\(^2\) bonds and optical excitation\(^{144}\).

![Figure 3.3. The main Raman bands for identification of carbon materials. (b) Raman scattering processes in graphene. Images adapted from\(^{145}\).](image)

G band and 2D band are the two distinct Raman features in almost all crystalline sp\(^2\) materials. The G band is a first-order scattering which is associated with stretching between adjacent sp\(^2\)-bonded carbon atoms, so its activation does not require 6-membered carbon rings\(^{144}\). It is positioned at \(\approx 1583\) cm\(^{-1}\) and is presented in any carbonaceous material containing sp\(^2\) bonds.

2D band (G’ band) is a second-order scattering positioned at 2670 cm\(^{-1}\), and the D band is a third characteristic peak at 1350 cm\(^{-1}\). D band arises due to radial stretching of hexagonal carbon rings in the lattice, and so requires a network of benzene rings to be activated\(^{144}\).

The double resonant processes in the 2D and D bands occur between the nonequivalent K points in graphene’s first BZ (Brillouin zone). In the case of the 2D mode, the scattering connects two zone-boundary phonons while the D mode connects a single phonon and a defect. Thus, the D band is absent in high-quality graphene that is defect free, and 2D(G’) band is therefore only present for well-ordered sp\(^2\) lattices, hence is the defining feature for identification of graphene and graphite.

In monolayer graphene the G’ band is well described using a single Lorentzian peak which is intense and narrow, with a full width at half maximum (FWHM) of 24 cm\(^{-1}\) – 30 cm\(^{-1}\).\(^{146,147}\) The D’ band, close to the G band frequency, is also a double-resonance process which acts as a measure of lattice disorder (Fig. 3.3a and 3.3b).

The 2D (G’) mode occurs from a combination of the zone-boundary in-plane longitudinal acoustic phonon and in-plane transverse optical phonon modes; characteristic Raman peaks are shown in Figure 3.3a. The order of a Raman band is defined by the number of scattering events involved, e.g. the G band is first order whereas the 2D band (two phonons) and D band (one phonon and a defect) are the second order.
In few-layer graphene with Bernal stacking, Raman spectra of graphene are sensitive to the number of layers. Ferrari et al. reported the change in a 2D band shape, frequency (position) and width (FWHM)\textsuperscript{147}. When the number of layers increases, 2D peak intensity reduces and becomes broader and upshifted in comparison to monolayer graphene. Also, the difference in the 2D shape between graphene and graphite is very noticeable (Fig. 3.4b).

![Figure 3.4](image)

Figure 3.4. (a) Variations in Raman spectra depending on the number of graphene layers and (b) Comparison of the Raman spectra of graphene and graphite. Images adapted from\textsuperscript{144}.

Another important factor that influences the position of the 2D Raman band is the choice of laser excitation energy, Fig. 3.5. The excitation energy also affects the shape of the 2D band as a function of the number of graphene layers. G-to-2D band intensity ratio increases with the number of graphene layers present, Fig. 3.4a\textsuperscript{144,147}. Also, due to the linear electron dispersion in graphene near the Fermi level, the D, D', and 2D bands are dispersive with different laser energies. They show a blue shift in their frequency with increasing the laser excitation energy.
Figure 3.5. (a) Measured 2D Raman band of different graphene layers showing the splitting of the 2D band which opens up as it goes from a monolayer (1-LG) to trilayer (3-LG) and then closes up as it goes from tetralayer (4-LG) to highly oriented pyrolytic graphite (HOPG). \(145\) (b) The change of the 2D peak shape as a function of the number of graphene layers are shown for 514 and 633 nm excitations, respectively. Image adapted from \(144,145\).

In summary, Raman spectroscopy reveals a tremendous amount of information about the properties of graphitic materials by probing the interplay between their electronic and vibrational structures. However, care does need to be taken with the interpretation of the spectra since different morphologies can give similar bands.

### 3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the most powerful and frequently used imaging techniques in materials science. It is used to obtain the information on morphology, structure and, if coupled with an EDX analyser, the composition of the studied solid materials. In SEM electrons are emitted from a source called the gun with energy typically in the range of 5 - 40 keV. When a focused electron beam with high acceleration voltage is irradiated on the surface of materials, secondary electrons can be knocked out from the atoms in the materials via inelastic scattering. Moreover, the incoming electrons can rebound as backscattered electrons due to elastic scattering (Fig. 3.6).
Electromagnetic lenses focus the electrons are like an optical microscope, and an aperture is used to limit the angular extent of the beam (Fig. 3.7). The beam is scanned across the sample in a raster fashion by electrical scan coils. At the sample, the beam is focused to a fine spot. Then, scattered electrons and secondary emitted electrons are detected at each point in the scan to build up an image sequentially. An SEM has a vacuum column to prevent electrons scattering in the air.

Figure 3.6. The interaction of the electron beam in SEM (source: Imaging and Microanalysis Course, University of Glasgow, 2011-2012).

Figure 3.7. Simplified schematic of essential parts of SEM. 

The interaction of the electron beam with the material is quite complex but essentially comprises the incident beam, with energy dependent on the accelerating voltage of the gun (5-40 keV), interacting with both the sample surface and the immediate subsurface, leading to the emission of two types of electrons (Fig. 3.7):

- Secondary electrons (SE), which are bound electrons excited by the incident electrons and ejected from the sample at relatively low energy.
- Backscattered electrons (BSE), which are the electrons from the incident beam scattered elastically with energies similar to the incident beam.

The detected SE are restricted to the area of the probe on the sample and the near-surface region of the material probed, thus resulting in high-resolution information of the specimen surface. On the other hand, BSE are sensitive to both topography and an atomic number of the material probed.

In graphene research, SEM is frequently used to characterise graphene grown on conductive substrates using the CVD method. It provides valuable information about graphene growth rates, sample coverage, nucleation density, grain size and morphology, but it cannot determine the exact number of graphene layers, providing only an estimate of the graphene layers’ uniformity.

However, the contrast in SEM images reveals qualitative information about the thickness of the deposited graphene, where darker parts are covered with a larger number of graphene layers and lighter parts are covered with less thick graphene.

Moreover, areas of more uniform contrast indicate a better graphene film coverage with more homogeneous graphene thickness and layer numbers. This contrast is due to the number of secondary electrons that are generated in the upper few nanometres of the sample surface.\textsuperscript{24,149,150}

In this thesis, SEM is mainly used to characterise the morphology of graphene, structure of graphene coatings, and corrosion morphology of metallic substrates.
3.4 GRAPHENE TRANSFER

CVD graphene is capable of large scale growth on Cu and other metals, but it is limited by graphene being bound to the conducting growth substrate. Graphene transfer from the growth substrate to a target substrate is pivotal for the application of graphene to both research and industry. Many methods have been developed in order to achieve a large area graphene transfer to target substrates with as few defects as possible\textsuperscript{155,151-153}.

Among several approaches to transfer the wet transfer with PMMA supported layer is commonly used so far. Figure 3.8 presents the simplified schematic of such a transfer.

![Figure 3.8. Schematic illustration of the wet-etching graphene transfer. Image adapted from\textsuperscript{154}.](image-url)
4. EXPERIMENTAL METHODS (CVD OF GRAPHENE ON COPPER)

4.1 CVD REACTOR

CVD systems are classified according to their working temperature, chamber pressure, the way that substrate is heated, reaction activation method, gas flow rate, deposition time and precursor nature\textsuperscript{155}.

All different types of CVD systems usually comprise the following basic units:

**Precursor delivery unit**: to deliver precursor materials, carrier and diluent gases to the reaction chamber in a controlled way.

**Energy source**: to provide the energy required to decompose the precursor molecule, and also to maintain temperature.

**Exhaust gas unit**: to remove unwanted reaction by-products and unused gases from the reaction chamber via pumps.

**Control unit**: to keep the volume rate of flowing gases constant throughout the process, also includes pressure gauges and temperature controllers.

In our experiment, we used the standard CVD setup with horizontal quartz reactor which can be moved in/out from the hot zone rapidly by sliding on the rails.

The gas delivery control unit (Yokogawa) comprises mass flow controls (MFC) of three gas lines, Methane (CH\textsubscript{4}), Hydrogen (H\textsubscript{2}) and Argon (Ar) which are all supplied at a high purity (99.95\%) (BOC, Guilford, UK) (Fig. 4.1).

All gases were delivered to the lab through high purity stainless steel lines, and each gas line had its own regulator showing the gas pressure inside the lines. This gas system provided a safer environment and ensured high levels of purity and clean gas supply. Each MFC was calibrated for a specific gas, with a maximum flow rate of 200 sccm for H\textsubscript{2}, 1000 sccm for Ar, and 100 sccm for CH\textsubscript{4}, so each gas has its manufacture designated and calibrated MFC.

The furnace was heated by silicon carbide elements with a maximum temperature of 1200°C and a 60 cm isothermal zone length. The reaction chamber is a fused silica tube 125 cm long, with 8 cm inner diameter, and 0.5 cm wall thickness.
The reactant gases were extracted from the reaction chamber through a two-stage rotary vane / turbomolecular pump. The pump has ultimate pressure of $2 \times 10^{-6}$ mbar, and it is connected to the chamber outlet via a flexible stainless steel tube to minimise the effect of pump vibration on the reactor.

### 4.2 SUBSTRATE PREPARATION AND GROWTH PROCESS

As part of initial training, I started with graphene growth on a widely investigated metal substrate - copper (Cu) foil. In this study, two different types of Cu foil were used from two suppliers: Goodfellow (Cambridge, UK) and Alfa Aesar (Haverhill, MA, USA), both with the thickness of 0.025 mm. Cu foil from Goodfellow was found to be a less suitable candidate for graphene growth because of the initial high polycrystallinity.

The foil surface shows consistent rolling defects/features which run parallel to each other, resembling scratches; these are the artefacts of the Cu foil manufacturing process, and they are unavoidable. Before the growth, the Cu foil was cleaned in acetone and isopropanol (IPA) to remove organic impurities; then the foil was etched in a 0.05 M solution of ammonium persulfate for 2 min to pre-oxidise the Cu surface. The latter procedure was conducted based on the literature report that oxygen on the Cu surface substantially decreased the graphene nucleation density by passivating Cu surface active sites\textsuperscript{156}.

The Cu foil sample was loaded into the reaction chamber and placed in the middle of the isothermal zone. The system was then evacuated to $10^{-5}$ mbar with further elevating the temperature. Cu foil was annealed in the furnace at 1000 °C in a hydrogen atmosphere. Inert
Gas also can be used to anneal, but usually argon might contain some percentage of oxygen, which is not desirable during annealing. Therefore, prior to every growth Cu foil was annealed for 30 min in 20 sccm of hydrogen. Annealing of the substrate is considered a vital process in CVD graphene growth since it reduces the native surface oxide and enlarges the grain size of Cu foil\textsuperscript{131}.

The CVD graphene growth follows directly after the annealing process, and the process begins as soon as methane is fed into the reaction chamber. In Table 1, the growth parameters and their ranges used to grow graphene on Cu foil are summarised. These ranges were determined based on literature studies and the limitations of our experimental setup. Approaching temperature higher than 1035°C, the vapour pressure of the Cu foil increases, thus, to avoid significant sublimation and step edge formation\textsuperscript{134} the pressure of the chamber was always kept at least five orders of magnitude greater than the vapour pressure of Cu.

Many of these process conditions have previously shown good results for graphene growth on a copper foil\textsuperscript{135}. After the growth phase, the methane flow is stopped, and the furnace is allowed to cool. Cooling the sample from the growth temperature to room temperature is carried out under a flowing hydrogen atmosphere to ensure no oxidation of the substrate occurs. I used two cooling regimes in my study: (i) fast cooling when the shell of the furnace is opened, or the hot furnace itself is slid away from the sample location and (ii) slow cooling when just methane is switched off, the hot furnace remains at the same position, and the substrate is allowed to cool naturally.

By introducing the argon flow, the chamber pressure is increased until it reaches the atmospheric pressure, then the chamber is opened, and the sample is unloaded for transferring and characterisation.
### Growth Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range of parameters</th>
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</thead>
<tbody>
<tr>
<td>Annealing temperature</td>
<td>1000 °C – 1035 °C</td>
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<tr>
<td>Annealing pressure</td>
<td>0.08 mbar</td>
</tr>
<tr>
<td>Annealing time</td>
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</tr>
<tr>
<td>Growth temperature</td>
<td>900 °C – 1035 °C</td>
</tr>
<tr>
<td>Growth pressure</td>
<td>$10^{-2} – 10^2$ mbar</td>
</tr>
<tr>
<td>Growth time</td>
<td>30 min – 4 hours</td>
</tr>
<tr>
<td>Partial pressure methane</td>
<td>0.0001 – 30 mbar</td>
</tr>
<tr>
<td>Partial pressure hydrogen</td>
<td>0.1 – 10 mbar</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>slow (25 °C /min) – fast (367 °C /min)</td>
</tr>
</tbody>
</table>

Table 3. The range of growth parameters used in this study.

It would be impractical to present the entire data set collected from each sample of Cu foil. Among the long list of recipes which was applied, the best results were obtained with a couple of them. Both of the recipes were originally created in the research group of Ruoff\textsuperscript{120,127} and with some modifications showed the best results. The first recipe allowed to grow high-quality continuous graphene sheet with minimum defects, while the second one resulted in monocrystalline graphene flakes with sizes up to 700 microns in diameter. The details and results will be presented later, and now are some of the main features which were obtained by probing the rest of the recipes.

While working with copper as a growth substrate for graphene, I focused not on the confirmation of well-known and widely studied growth parameters (temperature and pressure), but rather on probing and combining the published recipes to further investigate the mechanisms of graphene growth.

![Figure 4.2](image)

Figure 4.2. Influence of prolonged time on graphene coverage. Graphene grown at 1000°C, 100 mbar and flow of CH\textsubscript{4} - 5 sccm. (a) 20 min and (b) 60 min.
As was described above, the growth of graphene starts when carbon (C) species decompose from methane with the help of hydrogen and nucleate on the Cu surface. Nuclei grow to form islands and then domains that ideally should cover the metal surface in its entirety.\(^{21,97}\)

Figure 4.2 presents the optical images of partly covered Cu foils after two growth runs. The conditions for (a) and (b) panels presented are the same, but sample (b) was exposed to methane longer. Despite the prolonged time, graphene on the surface remained in the form of islands, likely due to a low flow of methane.

The full coverage cannot be achieved and graphene islands/domains never meet and create the continuous film for the following reasons:

(i) The methane flow is too low and the concentration of carbon-containing radicals is not enough even to start the nucleation process, and if it starts the full coverage is difficult to achieve.

(ii) When the exposed Cu surface area decreases, the graphene growth rate decreases dramatically because C species are supplied by the decomposition of methane catalysed by the available Cu surface. For example, in the work\(^ {98}\), it was found that the rate at which graphene covers Cu surface is proportional to the amount of uncovered Cu surface.

The increase of the domain size by decreasing the nucleation density in order to minimise the defect density induced by the growth boundaries can be achieved by controlling the pressure and hydrogen flow. It was found that a high ratio of the partial pressures of hydrogen and methane results in a smaller graphene grains\(^ {157}\) because too much hydrogen produce supersaturation of carbon species which in turn lead to multinucleation. Therefore it is expected that a higher methane flow would result in larger graphene grains. I found that good results are achieved for an H\(_2\)/CH\(_4\) ratio of 5, namely as-grown graphene shows better Raman features, i.e. higher 2D/G ratio and a lower D/G ratio. Figure 4.3 shows the comparative results of gas ratios. As it is clearly seen from the panel (a) the high ratio of H\(_2\)/CH\(_4\) leads not only to a higher nucleation density but also provokes the multilayer formation.

Even though the huge amount of publications is dedicated to the growth of graphene on Cu, reproducibility of results sometimes was very poor. The values of gas ratios and pressures I used presented in Figures 4.2 and 4.3, and in the literature vary greatly for a complete monolayer of graphene. Some of the papers report discontinuous growth using values that
reported continuous growth in other papers. Considering the many different CVD setups, it is likely that continuous growth is variable from system to system. The values used in this study to obtain unbroken growth (full monolayer coverage) are shown in comparison to the current literature and are summarised in Table 4.

![10 μm](image1)

**Figure 4.3.** Influence of the total pressure and partial pressure of hydrogen. (a) Pressure 50 mbar, CH₄:H₂ – 1:5, (b) pressure 1 mbar, CH₄:H₂ – 5:1. T – 1000 °C.

<table>
<thead>
<tr>
<th>Paper Author</th>
<th>PCH₄ (mbar)</th>
<th>PH₂ (mbar)</th>
<th>PAr (mbar)</th>
<th>Total P (mbar)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This Study</td>
<td>1.25</td>
<td>50</td>
<td>0</td>
<td>51.25</td>
<td>1000</td>
</tr>
<tr>
<td>Gao et al¹⁵⁸</td>
<td>3.32</td>
<td>0 - 498</td>
<td>498 - 996.8</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Sun et al¹⁵⁹</td>
<td>0.009</td>
<td>0.121</td>
<td>6.22</td>
<td>6.35</td>
<td>1000</td>
</tr>
<tr>
<td>Liu et al¹⁶⁰</td>
<td>80, 100, 120</td>
<td>60</td>
<td>860, 840, 820</td>
<td>1000</td>
<td>1030 - 1070</td>
</tr>
<tr>
<td>Levandorf et al¹⁶¹</td>
<td>11.91</td>
<td>2.72</td>
<td>0</td>
<td>14.63</td>
<td>1000</td>
</tr>
<tr>
<td>Li et al¹²⁰</td>
<td>0.665</td>
<td>0.133</td>
<td>0</td>
<td>53.2</td>
<td>1035</td>
</tr>
<tr>
<td>Kim et al¹⁶²</td>
<td>0.067</td>
<td>4.033</td>
<td>0</td>
<td>4.1</td>
<td>1000</td>
</tr>
<tr>
<td>Lee et al¹⁵³,¹⁶³</td>
<td>46.95</td>
<td>14.085</td>
<td>938.2</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Liu et al¹⁶³</td>
<td>13</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>980</td>
</tr>
<tr>
<td>Li et al¹⁷¹</td>
<td>0.629</td>
<td>0.036</td>
<td>0</td>
<td>0.665</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table 4. Comparison of partial pressures of gas species and temperatures used to obtain full monolayer graphene growth in this study and the literature.
4.3 Bi- and Multilayer Graphene Formation

The precise control on the number of graphene layers as well as the uniformity over a large area is still very challenging.

As it was reported, the mechanism of graphene growth on Cu is a surface-mediated process, and the growth is considered to be stopped when the catalytically active surface is not capable of providing active carbon\textsuperscript{164}. What drives the formation of the second layer? Is the 2\textsuperscript{nd} layer above or below the 1\textsuperscript{st} one? What are the carbon species directly feeding bilayer growth, and how do they form? The questions regarding the formation of more than one layer of graphene are remaining unclear.

Research work\textsuperscript{165} made a comparative analysis to investigate the effect of copper substrate thickness on the number of layers of the obtained graphene. It was shown that single layer coverage decreases with the increase of substrate thickness and, both bilayer and few-layer coverage increases correspondingly. Furthermore, surface coverage also changed with substrate thickness, i.e. larger surface coverage (~80 \%) was observed for thin substrates, while a smaller area coverage was recorded for thick substrates.

Also, at the growth temperatures close to the melting point of Cu, the possibility to get uniform monolayer is lower\textsuperscript{166}. The authors claimed that at permeating conditions (as they used high growth temperature – 1040°C) the solubility of carbon into the Cu could increase allowing more carbon to dissolve/diffuse into the Cu subsurface. However, in research work\textsuperscript{165} the growth temperature was always 1000°C.

The effect of copper substrate thickness on the number of graphene layers grown during CVD deposition has not been previously reported to the best of my knowledge. It was not the aim of my work to deepen the understanding of this mechanism, but I would like to note that this question worth further investigation.

The growth of graphene on Cu foil is believed to be a self-limiting process which, under the proper conditions, should result in monolayer graphene. However, the growth of graphene on Cu is often accompanied by thickness nonuniformity (bi-, and multilayers with a monolayer background). In work\textsuperscript{100} it was reported that graphene growth on Cu is not self-limiting under the higher methane concentration (even in the case of LPCVD \textasciitilde 625 mTorr = 0.8 mbar) resulting in large multilayer domains.
In the work\textsuperscript{167}, however, the growth parameter responsible for the formation of the next layer was reported to be a high temperature. The authors studied the influence of methane concentration and temperature on the formation of multilayer graphene. They found that second layer domains start to form not only after exceeding the critical point of methane introduced but also with the increasing of the growth temperature (the highest growth temperature they applied was 1070°C). It was concluded that there is a limited temperature window in which the graphene domains can maintain a monolayer structure. The limited window of applied values can be attributed not only to temperature, of course.

As it was noted above, the low pressure is the key parameter for the decreased density of nucleation. It also plays a role in the resulting number of layers and quality of graphene in general.

In my work, I checked the influence of both the total growth pressure and the partial pressure of methane during the growth on the graphene deposition.

Figure 4.4 presents the transferred after the growth graphene on Si/SiO\textsubscript{2}. All samples showed good continuity of the graphene layer and the coverage was complete. However, it is clearly seen that the sample (a) presented with multiple domains of multilayers of graphene (Raman mapping revealed the presence of bi-, tri- and more layers surrounded by monolayers). The density of defects (intensive D peak in Raman spectra) for sample (a) is much higher than for sample (b) which indicates a higher density of boundaries due to very small clusters of graphene. The second sample (b) was grown at the same conditions with the difference in pressure, and it is clear that the density of multilayers domains is much lower.

Samples (c) and (d) were grown at the same growth pressure, but the amount of methane was lower in the case of (d). Low pressure, therefore, can control not only the nucleation density but also the formation of multilayers. However, the influence of the partial pressure of CH\textsubscript{4} is more significant than the total pressure of the system.

In work\textsuperscript{168}, for example, the growth of the second graphene layer below the first one was demonstrated to be due to the diffusion of carbon atoms through the Cu bulk after a complete dehydrogenation of hydrocarbon molecules on the Cu surface.
4.4 Influence of the Position of the Growth Substrate

The ideal properties of graphene such as full coverage with low defect density, uniform thickness are desirable for all researchers in this field, but so far, there is no ideal recipe with certain windows of parameters. In my opinion, these windows should be found in every case individually since they widely vary from system to system.

The next important factor is the position of Cu foil inside the reaction chamber. It was already reported about an inferior growth of graphene on the bottom side of Cu foil\textsuperscript{169}. This is usually the reason why graphene from the top side is usually taken for characterisation and is etched from the bottom side during the wet transfer procedure. According to work\textsuperscript{170}, the gases flowing inside the reaction chamber during the growth are distributed such that
the bottom side of the Cu foil is less exposed to the C precursors as compared to the top side.

According to the theory of the boundary layer which is formed inside the reaction chamber during the growth process and which should be overcome in order for the active carbon species to reach the surface, it is not surprising to discover the distribution of graphene domains as illustrated in Fig 4.5.

![Graphene synthesis diagram](https://via.placeholder.com/150)

Figure 4.5. Upper panel - processes occurring at the mass transport during graphene synthesis using Cu as a catalyst in a CVD process (the case of the reaction fluxes under steady-state conditions)\(^\text{100}\). Lower panel - Optical micrographs of graphene observed at different spots along the gas flow direction showing an uneven distribution of gas carbon source during the growth\(^\text{138}\).

The lower density of graphene domains on Cu sites which are located farther from the main flow of gases can be understood, but the results I obtained using the bent foil are difficult to explain.
In my experiments for the convenience of loading and unloading the sample, I placed the growth substrate in a quartz boat, which in turn was put inside the quartz tube. The results of better growth on the top side of the foil in my work is fully consistent with the literature data. However, once I changed the position of Cu foil by simply bending it and placing as presented in Figure 4.6a, assuming that such position of Cu foil should be more available to the introduced precursor gases, I have got unexpected results. After the examination of the substrate, I found graphene domains only on one side of the bent foil.

![Figure 4.6. Influence of the substrate position on the resulted deposition of graphene. (a) position of Cu foil in the quartz boat. The boat was placed towards the gases flow, (b) incomplete graphene coverage on one side of the bent Cu foil.](image)

The fluid flow dynamics, heat transfer, and gas phase chemistry for the CVD reactor were studied and well described in works^{165,171}. When a sample immersed in a laminar gas flow, a region on the surface of the sample will form in which the flow velocity, temperature, and relative gas concentrations vary from the bulk flow^{172}. The volume of the affected space is known as the boundary/frictional/stagnant layer, and the nucleation on the substrate occurs via diffusion of the main flow through that boundary layer. It can be concluded that with negligible maximum entry length and a laminar uniform flow the formation of a boundary layer in the CVD set-up will not restrict repeatable graphene growth when identical growth conditions are used^{9}. Based on the described above model, it was unexpected to get the distribution of graphene covering as in Fig. 4.6b. Indeed, such results are related to the fluid dynamics of the system and raise the question about the real gas flows inside the chamber during the growth.
4.5 Modification of growth recipes

4.5.1 First growth recipe

Regarding the choice of the best recipe to obtain high-quality monolayer of graphene with minimum defects, I chose to follow Li et al. study\textsuperscript{120}. They studied the effect of growth parameters such as temperature, methane flow rate, and methane partial pressure on the domain sizes of the grown graphene.

Figure 4.8. Two-step process flow of continuous graphene films with large domains\textsuperscript{120}.

Figure 4.8 outlines the two-step process. For the first step, the high temperature and low methane amount (low flow rate and, consequently, low partial pressure) are required. Such conditions allow growing large graphene domains. If the process remains at this step, the graphene layer is not likely to become continuous. On the second step, the methane flow and the partial pressure were increased, which led to further growth of graphene domains and almost full coverage. As it was investigated by Raman spectroscopy, applying this method, \( \approx 80\% \) coverage of copper by graphene was obtained. It is important to note that for a given temperature and partial pressure conditions, once the carbon nuclei density is set, no significant new graphene nuclei are formed and subsequent changes in growth conditions only affect the graphene growth rate.

Based on the observations of work\textsuperscript{120}, it was decided to apply the two-step approach to grow graphene with large domain sizes. The only difference in my case was that I made this process not isothermal: on the second step, the temperature was slightly decreased alongside increasing the methane flow rate and pressure. High temperature is necessary at
the beginning - at the nucleation stage in order to initiate the growth. After that, the growth process is governed by rate flux of carbon species and by the surface reactions.

<table>
<thead>
<tr>
<th>Growth parameters</th>
<th>Value used</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Growth temperature</strong></td>
<td>1035°C – 1000°C</td>
</tr>
<tr>
<td><strong>Growth pressure</strong></td>
<td>100 mbar ~ 75 Torr</td>
</tr>
<tr>
<td><strong>Growth time</strong></td>
<td>40 min</td>
</tr>
<tr>
<td><strong>H₂ flow rate</strong></td>
<td>40 sccm</td>
</tr>
<tr>
<td><strong>H₂ partial pressure</strong></td>
<td>60 mbar</td>
</tr>
<tr>
<td><strong>CH₄ flow rate</strong></td>
<td>5 sccm – 10 sccm</td>
</tr>
<tr>
<td><strong>CH₄ partial pressure</strong></td>
<td>12 mbar – 15 mbar</td>
</tr>
<tr>
<td><strong>Cooling rate</strong></td>
<td>Fast cooling</td>
</tr>
</tbody>
</table>

Table 5. Growth parameters used in the first growth recipe.

The influences of growth temperature, CH₄ flow rate and annealing temperature were intensively studied to synthesise high-quality graphene at ambient pressure. In work, the results showed that higher annealing temperature with respect to growth temperature increases the chances to deposit a monolayer of graphene.

Figure 4.9 presents the optical image in dark field mode and corresponding Raman spectra of the obtained graphene. One can see that the surface of Cu foil is continuously covered by graphene and Raman features correspond to the monolayer of graphene.

![Figure 4.9](image)

Figure 4.9. Results of obtained CVD graphene on Cu using the first growth recipe. Left panel - optical image in dark field mode showing the complete surface coverage and right panel - Raman spectrum with main features indicating the ideal single layer.
After the growth, graphene was transferred on Si/SiO$_2$ and characterised by Raman spectroscopy. The resulted graphene was of high quality as revealed by Raman and found its application in the work$^{173}$, results of which are presented in the next chapter.

4.5.2 Second growth recipe

Next, I used the second growth recipe, where lower pressure (compare to the first recipe) was applied. The recipe was adapted from work$^{174}$, but this method with using Cu envelopes (or enclosures) originates from the group of Ruoff as well$^{175}$. The Cu foil was etched in 0.05 M solution of ammonium persulfate for 3 min to clean and peroxidase the surface. After that foil was rinsed in deionised water using the ultrasonic bath and dried in compressed air. From Cu foil then was created the envelope with tight edges to prevent the evaporation of Cu from the inside surfaces during the growth. To avoid the sintering of the foil sides, inside the envelope, a piece of quartz (2x1 cm) was placed. Before the growth, the Cu envelope was annealed in hydrogen for 20 min.

<table>
<thead>
<tr>
<th>Growth parameters</th>
<th>Value used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth temperature</td>
<td>1035°C</td>
</tr>
<tr>
<td>Growth pressure</td>
<td>10$^{-2}$ mbar</td>
</tr>
<tr>
<td>Growth time</td>
<td>4 hours</td>
</tr>
<tr>
<td>$\text{H}_2$ flow rate</td>
<td>35 sccm</td>
</tr>
<tr>
<td>$\text{CH}_4$ flow rate</td>
<td>3.5 sccm</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>Slow cooling</td>
</tr>
</tbody>
</table>

Table 6. Growth parameters used in the second growth recipe.

The resulted graphene flakes after the growth are presented in Fig. 4.10. The big graphene flakes with diameters up to 750 microns were found on both sides of the foil. It is interesting to note, that all of them (or at least those I have checked by Raman spectroscopy) were bilayers on the external side. Inside flakes were bi- and tri-layered.
The next interesting fact is that the graphene flakes tend to form hexagons even if they grow by dendritic pathways (Fig. 4.10b – the first layer of graphene), the second layer covers the previous one by a solid hexagon. The gas flows during the growth remained unchanged, so it is unclear why the second layer grew via a different pathway.

Also, it is worth noting that on the outer side of Cu, alongside with big flakes, I found small nucleation dots (yellow dots around the big flake) which were small graphene dots as revealed by Raman. These dots did not continue the growth and remained the same in size. That was probably because of Cu evaporation, which can suggest that the formation of big flakes on the external side happens through the diffusion of carbon species from the inside. Additionally, the layers share the same nucleation centre on the outside flakes and have different centres on the inside flakes of the foil. Work\textsuperscript{176} studied the growth of bilayer and multilayer graphene on copper by isotope labelling of the methane precursor and authors found that graphene adlayers share the same nucleation centres and all adlayers nucleating in one place have the same edge termination. Also, in the mentioned work, it was reported that adlayer graphene forms between the first graphene layer and its substrate.

The question is, how did graphene flakes deposit on the outer side of the copper foil? Was it the direct deposition of methane or carbon diffused from the inside of the envelope?

Fang et al. studied the effect of copper substrate thickness on BLG formation on the outside surface of a copper enclosure\textsuperscript{177}. Their results confirmed that by reducing substrate thickness from 125 \( \mu \text{m} \) to 57 \( \mu \text{m} \), more carbon diffusion occurs from the inside to the outside surface, which leads to an increase in coverage of trilayer and tetralayer films.
4.6 CVD GRAPHENE FROM A LIQUID SOURCE

Methane (CH₄), acetylene (C₂H₂) and ethylene (C₂H₄) represent the typical gaseous carbon precursors used for graphene CVD synthesis. As it was mentioned earlier, carbon precursors are not limited by gases. Liquid precursor based growth can help in realising graphene doping because nitrogen- and boron-containing organic solvents (pyridine, triethylborane) are inexpensive and easy to use, whereas organic gases containing dopant atoms are rather uncommon.

A recent publication by Seo et al. has been touted to be the solution for low-cost synthesis of graphene. There, soybean oil was used as the carbon source for graphene synthesis. Other than soybean oil, there have been several other complex carbon precursors reported in the field of graphene synthesis such as waste chicken fat and commercial palm oil. In the work the growth from less expensive, even with a negative value, carbon sources, such as food, insects, and waste, was demonstrated, which can be used without purification to grow high-quality monolayer graphene directly on the backside of Cu foils under the H₂/Ar flow.Basically, any carbon-containing source can become a precursor for graphene growth; even asphalt can become another promising candidate.

The mechanism of graphene formation requires the active carbon radicals to start creating clusters and grow into graphene domains on the substrate surface. Using the liquid precursors requires to convert the liquid into gaseous form before it reaches the active metal catalyst region. Usually, it requires lower temperatures. For example, liquid precursors such as benzene and pyridine can synthesise graphene at around 300°C. Additionally, graphene can be doped by other elements which precursor contains. Xue et al. demonstrated the synthesis of highly N-doped graphene at temperatures as low as 300°C by using pyridine (C₅H₅N) as carbon precursor.

To the best of my knowledge, among the exotic sources for carbon precursors for graphene growth, no part of human tissue nor liquids ever been tried to use. Therefore, it would be an interesting idea to try to use human blood as a source of carbon. However, first, a brief introduction to the blood and containing elements is required.

Blood is a complex mixture of compounds: red and white blood cells which are suspended in a liquid – plasma. It is slightly denser and approximately 3-4 times more viscous than water.
Chemically, plasma and cells consist of proteins and hydrocarbons. Work\textsuperscript{184} reported many representatives of the periodic table in blood. For example, elements of blood plasma - Ag, Ca, Cu, In, Li, Na, Se, Si, Sr, and elements of blood cells - Fe, K, Mn, Ni, V, Zn. Many of them, indeed, in trace amounts and mostly blood is presented by iron, carbon, nitrogen, oxygen and hydrogen.

Haemoglobin in red blood cells carries oxygen for the respiration by means of an iron atom that is a part of its structure, Fig. 4.11b. Haemoglobin is made up of four protein molecules (globulin chains) that are connected together. Each globulin chain contains an important iron-containing porphyrin compound termed haem. Embedded within the haem compound is an iron atom that is vital in transporting oxygen and carbon dioxide in our blood. The iron contained in haemoglobin is also responsible for the red colour of blood.

The idea was to grow graphene using human blood. The person who provided his blood to test the possibility to grow graphene from a liquid source was the discoverer of graphene - my supervisor Kostya Novoselov (Fig. 4.12).
Cu foil was pre-treated in ammonium persulfate before covering half of it by the liquid source. Then the foil was placed into a furnace, and first, the sample was heated in a vacuum for 1 hour to evaporate water and to remove excess moisture. After that, Ar and H₂ in a ratio of 50:50 sccm were introduced into the reaction chamber. The growth was conducted at 1000°C and pressure 100 mbar.

The first attempt when Cu foil was flat, however, was not successful – we did not find any traces of graphene, only amorphous carbon. When it was decided to use the “enclosure” approach and consequently the lower growth pressure. After 2 hours of exposing to Ar and H₂ without methane and any other carbon sources but blood, the attempt was successful. Cu envelope was covered by graphene from the inside (Fig. 4.13)
The presence of graphene was revealed by optical microscopy both in ordinary and in a dark field mode, Fig. 4.13a, b. Resulted graphene was highly inhomogeneous with many regions of amorphous carbon, but the areas of ideal monolayer graphene were found as well. Non-uniform deposition of resulted graphene was, indeed, due to non-uniform Cu foil coverage by blood. The different thickness coverage resulted in uneven evaporation of water from the foil, and the thicker regions were mostly covered by amorphous carbon.

To measure the electrical properties of blood-grown graphene and to compare them with the properties of exfoliated graphene, field-effect transistors were fabricated. To this end, CVD-grown graphene was transferred onto an oxidised silicon substrate (SiO$_2$ thickness 300 nm) using bubble transfer method$^{50}$. Metal contacts were patterned using electron beam lithography followed by electron beam evaporation of 3 nm Cr and 50 nm Au and a subsequent lift-off (Figure 4.14 shows the device micrograph). To perform the measurements, the device was cut into a chip carrier, wire-bonded and placed into a helium flow cryostat fitted with variable temperature insert and a superconducting magnet.

![Optical micrograph of the blood-grown graphene device.](image)

Figure 4.14. Optical micrograph of the blood-grown graphene device.
Measurements of (a) resistivity and (b) magnetoresistance of the device shown in Fig. 4.14. Figure 4.15a plots the four-terminal resistivity $\rho_{xx}$ as a function of back gate voltage $V_{bg}$. The resistivity peak is shifted to +40V, suggesting strong hole doping of the graphene. There is also a visible hysteresis in the $\rho_{xx}$–$V_{bg}$ behaviour probably originating from the charging-discharging of trapped impurities. Field effect mobility extracted from $\rho_{xx}$–$V_{bg}$ amounts to $\approx 7400 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is a typical value for graphene on silicon devices. Encapsulation of graphene should potentially significantly improve the electronic quality of this CVD-grown graphene.

Surprisingly, we found strong negative magnetoresistance in the device persisting up to fields of 10 Tesla (Fig. 4.15b). This suggests the presence of strong disorder. At small magnetic fields, the negative magnetoresistance deviates from linear behaviour; this might signify the presence of weak localisation, which can be attributed to intervalley scattering possibly due to the presence of $sp^3$ defects and other scattering centres.

These are the preliminary results, and further investigation is required: for instance, fabrication of hBN-encapsulated device might help to differentiate the disorder induced by Si/SiO$_2$ substrate from the scattering originating from CVD-growth due to the presence of Fe atoms in blood source.

### 4.7 Model of Graphene Growth

The following assumed mechanism was first proposed by Kim et al. and then studied and supplemented in work.

\[ eV \approx \text{energy of Fe atom} \]
After the Cu foil exposed to methane gas and subsurface is reached by active carbon species followed by dehydrogenation of methane, the surface can become (i) under-saturated, (ii) saturated, or (iii) super-saturated with C, H and C,H\textsubscript{x}. Depending on the degree of saturation, graphene will nucleate (or not) and form (or not) grains which grow into each other, forming a continuous layer.

If Cu surface is under-saturated with C adatoms, consequently graphene cannot nucleate even though the C species are present in the environment.

If Cu surface has enough C and C_H\textsubscript{x} to start the graphene nucleation, these nucleations grow into graphene grains but are restricted in size due to insufficient amounts of C and C_H\textsubscript{x} reacting with the available Cu surface to continue the growth into a continuous layer.

If the CVD environment is such that the activation/reaction rate between CH\textsubscript{4} and Cu is increased enough for adsorption to dominate, then graphene grains can continuously grow until the catalyst surface is covered\textsuperscript{118}.

The schematic illustration of the proposed mechanism is presented in Figure 4.16.

![Schematic possible mechanism highlighting the basic CVD growth mechanisms on Cu. Image adapted from\textsuperscript{9}.](image-url)
4.8 Conclusions

Based on the analysed literature data and my results, I can make some brief conclusions about the mechanism of graphene formation on Cu foil. In order to cover the whole substrate surface by the high-quality graphene (with minimum defects due to large graphene domains), the following conditions after the thorough pre-treatment of the Cu should be considered. The relatively high temperature should be applied. Low temperature (< 800°C) induces the multinucleation of graphene, whereas the too high temperature (> 1050°C) can lead to the desorption of the active carbon species. Relatively low pressure is favourable for a monolayer of graphene. The growth pressure is close to UHV in tandem with high temperature can lead to the evaporation of Cu foil. The ratio of \( \text{CH}_4/\text{H}_2 \) vary from system to system and should be found in each case individually. It is necessary to find the balance between two limiting conditions: when (i) too much methane leads to a multilayer formation, and (ii) too much hydrogen etches the deposited graphene. The certain position of the substrate can lead to unexpected coverage of Cu foil by graphene. Therefore, the attention should be paid on the position of foil with respect to gases flow in the reaction chamber.
5. **GRAPHENE-BASED FIELD EFFECT PHOTOTRANSISTORS**

The work is done in collaboration with the research group at the School of Physics and Astronomy of the University of Nottingham and was published in. Contribution: provided CVD graphene samples, performed Raman experiments, assisted in the writing.

5.1 **INTRODUCTION**

Atomically thin van der Waals (vdW) crystals and their heterostructures offer interesting prospects to control the behaviour of electronic charges at the interfaces between different materials and to create multi-functional devices for integration with optoelectronic technologies. VdW crystals have strong covalent bonds within the two-dimensional atomic planes and weak vdW forces between the atomic (or molecular) planes. These features allow to make stable films down to a monolayer thickness and to realise a range of multilayer structures, overcoming limitations of traditional compound semiconductors (e.g. incompatibility or imperfect interfaces due to lattice mismatch). For instance, a broad range of 2D materials is currently being explored, including semimetal graphene, insulator hexagonal boron nitride (hBN), semiconductor black phosphorus (bP), and various transition metal dichalcogenides (TMDCs, e.g., MoS$_2$, WS$_2$, etc.)

Among these 2D materials, the post-transition metal monochalcogenides, such as InSe, are currently under more attention. Interestingly, InSe can act as an electrically/optically active layer to dope and photosensitise a contiguous graphene layer, and to induce a “giant” quantum Hall (QH) plateaus. These phenomena involve a charge transfer at the interface between InSe and graphene offering prospects towards new optoelectronic applications.

In this chapter, we present the effects of light on the transport properties of field effect phototransistors made from CVD-grown monolayer graphene partially covered with n-type InSe. It was demonstrated using magneto-transport measurements that the absorption of light by the transferred InSe flake induces: (i) gate-tuneable changes of the resistivity of CVD-grown graphene; (ii) light- and gate-tunable sign reversal of the Hall resistance in the QH regime. These two effects arise from the sensitivity of graphene conductivity to mobile charges that are photogenerated in the InSe flake and transferred across the interface to graphene. Observed light-induced charge transfer offers an effective method to precisely control carrier density in the InSe-capped graphene. The optically-induced transition from the hole- to electron-type electrical currents was achieved over a broad range of gate voltages, highlighting the potential for quantum metrology, photo-sensors, and photo-switches.
5.2 **EXPERIMENTAL METHODS**

Graphene monolayer was grown via CVD on a copper foil substrate (the first modified growth recipe) and was then transferred to a SiO$_2$/p-Si substrate (285 nm of SiO$_2$). The graphene multi-terminal Hall bar mesa was formed using electron-beam lithography and oxygen/argon reactive ion etching, followed by a deposition of Au/Ti electrodes (100/10 nm). High-quality InSe flakes were exfoliated from a Bridgman-grown InSe crystal onto a polydimethylsiloxane membrane. A selected InSe flake was then transferred onto the graphene Hall bar, capping a section of the graphene channel while avoiding contacts with Au/Ti electrodes. Exfoliated InSe flakes capped with hBN were also integrated into two-terminal planar device structures incorporating graphene electrodes.

The magneto-transport measurements were performed with the device mounted inside a cryostat equipped with a superconducting magnet capable of reaching magnetic fields $B$ up to 14 T or using a resistive magnet with $B$ up to 25 T and over a range of gate voltages, $V_g$, applied between the graphene and the Si substrate. For the magneto-transport experiments under optical illumination, an unfocused He-Ne laser beam (wavelength $\lambda = 632.8$ nm, power, $P$, up to 13 mW mm$^{-2}$, and spot diameter $d \approx 1$ mm) was used.

5.3 **TRANSPORT MEASUREMENTS OF GRAPHENE–INSE PHOTOTRANSISTORS**

Figure 5.1a shows an optical micrograph of InSe/graphene phototransistor, note the InSe flake covering half of the graphene Hall bar. The two sections of the device comprising uncapped and InSe-capped graphene are in a series resistance configuration with the same electrical current, $I$, flowing through both of them, Figure 5.1b. Transport measurements were performed in two modes: (i) in dark, and (ii) with the device uniformly illuminated by an unfocused He-Ne laser beam with a photon energy, $h\nu = 1.96$ eV, in excess of the bandgap energy of bulk InSe, $E_g = 1.26$ eV at 300 K.

The $V_g$-dependence of the low ($T = 2$ K) and room temperature ($T = 300$ K) resistance, $R_{\infty}$, of the uncapped and InSe-capped graphene measured at zero magnetic field in dark is shown by the black dashed lines in Figure 5.1c. For uncapped graphene, $R_{\infty}$ reaches a maximum at a positive gate voltage, $V_g = +21$ V at $T = 2$ K; thus the graphene is $p$-doped at $V_g = 0$ V with $p = 1.6 \times 10^{12}$ cm$^{-2}$. For InSe-capped graphene, the maximum of $R_{\infty}(V_g)$ occurs at somewhat smaller $V_g = +7$ V, shifted by $\Delta V_g = -14$ V relative to the uncapped graphene peak, thus corresponding to a reduced hole density. The $R_{\infty}(V_g)$ curve for the uncapped graphene section of the Hall bar does not change when its surface is laser-illuminated. In contrast, for
InSe-capped graphene, the maximum of $R_{xx}(V_g)$ shifts towards lower gate voltages at both low and room temperatures (red curves in Figure 5.1c). This shift, $\Delta V_g$, is proportional to the light intensity at low levels, but saturates to $\Delta V_g \approx -6 \, \text{V}$ for $P > 10 \, \text{mW mm}^{-2}$.

![Figure 5.1](image.png)

Figure 5.1. Graphene transistors photosensitised with InSe. a) Optical image and b) schematics of a Hall bar containing uncapped and InSe-capped graphene. The thickness of the InSe layer is 50 nm, as measured by atomic force microscopy. Devices with different layer thickness down to $\approx 10$ nm show similar behaviour. c) Resistance $R_{xx}$ versus gate voltage $V_g$ ($B = 0 \, \text{T}$ and $I = 0.5 \, \mu\text{A}$) without (black curves) and with illumination (red curves; $\lambda = 633 \, \text{nm}$ and $P = 9 \, \text{mW mm}^{-2}$) for the uncapped graphene (G) and InSe-capped graphene (InSe/G). Top: $T = 2 \, \text{K}$; bottom: $T = 300 \, \text{K}$. $V_i$ and $V_o$ denote the peak position of the $R_{xx}(V_g)$ curves under illumination and in darkness, respectively. d) Dependence on the gate voltage $V_g$ of the change in the resistance, $\Delta R_{xx}$, of the InSe-capped section of the graphene Hall bar after illumination.

The photosensitivity of the InSe-capped graphene section of the device is illustrated in more detail in Figure 5.1d, which shows the gate voltage dependence of light-induced $\Delta R_{xx} = R_{xx}(\text{light}) - R_{xx}(\text{dark})$, at $T = 2 \, \text{K}$. $\Delta R_{xx}$ has a maximum at a gate voltage $V_i \approx 0 \, \text{V}$, passes through zero at a gate voltage $V_F \approx +6 \, \text{V}$, and changes sign with a minimum at $V_D \approx +10 \, \text{V}$. 
The values of $V_D$ and $V_L$ correspond to the peak positions of the $R_{xx}(V_g)$ curves in dark and under laser illumination, respectively (Figure 5.1c). Figure 5.1 demonstrates that in darkness InSe-capping of the CVD-grown graphene significantly increases the electron density in the graphene layer. Under illumination, the density of electrons in the InSe-capped graphene increases even further. In particular, the similar form of the $R_{xx}(V_g)$ curves at low and room temperatures indicates a relatively weak contribution of phonon scattering to the mobility of charge carriers. This behaviour can be accounted for by the dominant contribution of carrier scattering by negatively charged acceptor impurities in our CVD graphene\textsuperscript{195}. Further, the gate-dependent quantum Hall effect measurements were used to examine how the photogenerated electrons are distributed between the InSe and graphene layers in the InSe/graphene heterostructure.

5.4 PHOTOQUANTUM HALL EFFECT

The effects of light on the Hall resistance, $R_{xy}$, and its dependence on $V_g$ are shown in Figure 5.2a for various magnetic fields, $B$, and $T = 2$ K. For gate voltages in the range $V_L < V_g < V_D$ (see coloured areas of the top three panels in Fig. 5.2), the optical excitation induces a sign reversal of the Hall voltage and of the QH plateau, $R_{xy} = h/ve^2$, where $v = 2$ is the graphene Landau level (LL) filling factor. Thus, illumination induces a transition from a hole-to an electron-carrier current in the graphene layer over an extended range of gate voltages (Figure 5.2b).

Figure 5.3 plots Hall resistance $R_{xy}$ under illumination as a function of magnetic field $B$ applied perpendicular to the sample plane. The large negative charge in the InSe-capped graphene with increasing positive gate voltage and increasing light intensity causes the asymmetric distribution of LL-features and QH plateaux relative to the peak in $R_{xx}(V_g)$. In particular, over a range of gate biases, the QH plateau extends to high $B$. For example, at $V_g = 7.5$ V and $V_g = -6.0$ V, the QH plateau extends from $B \approx 5$ to 14 T at $T = 2$ K, corresponding to an increase in sheet density of $\approx 5 \times 10^{11}$ cm$^{-2}$ (Figure 5.3a), and persists over a wide range of temperatures (Figure 5.3b). This behaviour was observed for several devices although the gate voltages at which the QH resistance plateau occurs vary slightly among the samples. The extended $v = 2$ QH plateau arises from the “pinning” of the chemical potential in the energy gap between the Landau levels. This is facilitated by the close alignment of the conduction band edge of InSe with the neutrality (Dirac) point of graphene: the electron affinity of graphene ($\chi_{Gr} = 4.5$ eV) is only slightly smaller than that of InSe ($\chi_{InSe} = 4.6$ eV)\textsuperscript{195}. 

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Figure 5.2. Landau level quantisation. a) Hall resistance, $R_{xy}$, of InSe-capped graphene versus gate voltage, $V_g$, in darkness (dashed line) and under illumination (continuous line) at $T = 2$ K and $B = 5$, 10, and 14T ($I = 0.5$ µA, $\lambda = 633$ nm, and $P = 9$ mW mm$^{-2}$). The coloured areas identify the range of gate voltages for which light reverses the $R_{xy}$ sign. b) Landau level quantisation in graphene and schematics of the Fermi level shifts between the lower to the upper parts of the Dirac cone under the illumination, leading to the sign reversal of $R_{xy}$ as shown in the upper panels.
Figure 5.3. Photoquantum Hall Effect. a) Hall resistance, $R_{xy}$, of InSe-capped graphene vs magnetic field $B$ at $T = 2$ K and different gate voltages $V_g$ under the laser illumination ($I = 0.5$ µA, $\lambda = 633$ nm, and $P = 9$ mW mm$^{-2}$). b) $R_{xy}$ of InSe-capped graphene versus $B$ under illumination at different temperatures, and $V_g = -6.0$ V.

The extended QH plateau presented here is comparable to that observed in epitaxially grown graphene by the thermal decomposition of the surface layer of SiC$^{197,198}$. The phenomenon has been explained in terms of the transfer of charge carriers, between the graphene layer and defects in the adjacent SiC substrate$^{199}$. This demonstrates that a similar process occurs between graphene and donors in the InSe flake. Thus the 0th Landau level at the graphene neutrality point remains filled when its degeneracy increases with increasing $B$. The results prove that this effect can be controlled by both the gate effect and light. Although the observed QH plateau in $R_{xy}$ becomes weaker with increasing temperature, it can still be seen even up to temperatures of $T = 200$ K at $B = 14$T, Figure 5.3b. The quenching of the QH plateau at higher $T$ can be attributed to the thermally-driven ionisation of electrons from the donor states into the conduction band of the InSe, leading to thermally-activated parallel conduction in InSe flake.
5.5 **Conclusions**

Novel hybrid InSe/graphene phototransistor devices were demonstrated. Mounting the InSe/graphene heterostructure on SiO$_2$/Si substrate enables the devices in which the electronic properties of graphene can be tuned by a combination of electrostatic field effect and the transfer of photoexcited charge carriers across the InSe-graphene interface. This allows the Fermi energy of the graphene layer to be fine-tuned across the Dirac point, thus achieving either $n$- or $p$-type conduction. The light-induced charge transfer also induces a reversal of the sign of the Hall voltage and of the $h/2e^2$ quantum Hall plateau, which extends over a wide range of applied magnetic fields and temperatures. The hybrid phototransistor devices are made by a simple microfabrication process and offer a flexible route to the integration with existing silicon manufacturing technologies. Future research can include the study of the charge transfer in other multilayered heterostructures, for instance in InSe/hBN/graphene stack, to explore controlled charge transfer between graphene and InSe through a tunnelling hBN barrier.
6. CVD OF GRAPHENE ON TA FOIL

This work was carried without any collaboration, all parts of the work were made by myself except the fabrication of graphene-based FET. This study comprises results included in the publication\textsuperscript{200}.

6.1 INTRODUCTION

It is highly beneficial to expand the growth of graphene on other metal substrates to use its barrier properties\textsuperscript{82,201}. For instance, in the next sections, the growth of graphene on such metals as tantalum (Ta) and rhenium (Re) will be presented. Such materials are used as targets in the production of radioactive ion beams\textsuperscript{1,202}, by irradiation (typically by protons). It is, however, often required to protect such targets from ageing and oxidation. Graphene would be an ideal protection layer due to its monoatomic thickness (which significantly reduces the probability of particle-layer interaction) and because the kinetic energy distribution of the nuclear recoil fragments is such that graphene has no impact on it.

Graphene growth on well-known and well-studied catalysts as Cu and Ni is usually conducted at $\approx 1000^\circ C$. Apart from Cu and Ni, other catalysts such as Pt, Ru, Ir, Co, Pd have been used in the graphene CVD, but for all of these materials, the growth temperatures were around $1000^\circ C$. Therefore, graphene growth at higher temperatures is rarely reported. In conventional CVD setup with a quartz reaction tube, it is not possible to elevate the temperature higher than $1200^\circ C$, which is limited by the melting point of silicon oxide. So, usually, the growth at $1200^\circ C$ and higher is conducted either in setups with a ceramic tube or in cold wall CVD systems where high temperature is reached by internal heating elements or infrared sources\textsuperscript{203}. In this chapter, I investigate the growth of graphene on refractory metal with an extremely high melting point – tantalum.

Carbon solubility in tantalum is higher than that in Cu but lower than in Ni. Moreover, Ta is a well-known carbide forming metal because of its great affinity to carbon. Affinity can be explained by the presence of unfilled d-shell, Ta $[Ar^5d^34s^2]$ as compared to Cu $[Ar^3d^{10}4s^1]$, which has the most stable configuration and can only provide catalytical activity forming soft bonds with carbon on the surface.

Tantalum, like many TM (Ni, Co and Fe) with unfilled d-shell, forms stable (TaC) and metastable (Ta$_2$C) carbides with carbon and the formed metacarbide promotes the precipitation of carbon, allowing carbon to diffuse out of Ta/Ta$_2$C\textsuperscript{204}. 

6.2 **SUBSTRATE PREPARATION**

In my experiments, I used the same CVD setup described in the previous chapters. The tantalum foil (99.8% purity, thickness 0.2 mm) purchased from Goodfellow Cambridge, UK Ltd. was used for CVD of graphene. As received tantalum foil was not free from impurities and also always covered by a passivating oxide film. The electropolishing in sulfuric acid-methanol electrolyte\(^\text{205}\) was made to smoothen the surface by the anodic dissolution of an oxide film and to clean from a variety of factory impurities. Figure 6.1 presents the Ta surface after electropolishing procedure. From the surface, the oxide layer was quite rapidly removed, showing the polycrystallinity of Ta foil underneath, Fig. 6.1.

![Optical and SEM images of Ta foil after electropolishing procedure.](image)

**Figure 6.1.** Optical and SEM images of Ta foil after electropolishing procedure. (a) Optical micrograph illustrating the polycrystallinity of Ta foil, (b) SEM image showing the difference in contrast between the crystals, (c) and (d) magnified SEM images from (b) etched crystals presenting the difference in polishing depending on the crystal orientation.

The crystallites were presented by darker and lighter in colour areas, and as it is seen from the picture, the foil was polished differently with respect to crystal orientations. I found that
graphene growth on tantalum foil with oxide allowed for better quality graphene, Fig. 6.2. In fact, on electropolished foil, only carbide and negligible presence of amorphous carbon were found. It might be attributed to an excellent catalytic performance of tantalum pentoxide\textsuperscript{206}, which helps methane cracking to obtain atomic carbon. In the rest of the study, I concentrate on our results obtained on the tantalum foil with oxide.

![Image of Optical images and Raman data demonstrating the optimal conditions for the growth of graphene on tantalum foil.](image)

**Figure 6.2.** Optical images and Raman data demonstrating the optimal conditions for the growth of graphene on tantalum foil. (a) and (b) Optical images of tantalum surface and Raman spectra after the graphene growth process on pristine and etched foils, correspondingly. Insets: scale bar 50 µm. Image from.\textsuperscript{200}

### 6.3 Influence of Gases

Finding the appropriate ratio of CH\textsubscript{4}:H\textsubscript{2}, as well as the proper amount of hydrogen during preheating and annealing step, was very important in this part of the work. Hydrogen has a great reactivity with tantalum easily forming hydrides. It can migrate into the bulk of the metal changing the lattice parameters. As it was reported, the absolute values of the diffusion coefficient of hydrogen into tantalum is comparable and even larger than diffusion coefficients in liquids or dense gases\textsuperscript{207}.

When the ratio of H\textsubscript{2}:CH\textsubscript{4} was higher than one, the surface of tantalum foil became rough, brittle, corroded by tantalum hydride. However, too high amount of CH\textsubscript{4} showed an almost similar surface reaction. Samples after the growth run showed severe deformation, Fig. 6.3. Raman analysis identified the deposited material in (b) as a soft amorphous carbon, in (c) as tantalum hydride.
Figure 6.3. Optical images of Ta foil: (a) before growth, (b) after applying an excessive amount of methane, and (c) hydrogen. Scale bars are 20 µm.

In order to choose the optimum hydrogen to methane ratio for growth, a series of tests have been performed. Hydrogen plays several roles in graphene formation on Ta: it reduces tantalum oxide, promotes carbon diffusion into tantalum\(^{208}\) (thus stimulating the formation of TaC phase), and etches the low-coordinated carbon. After a series of tests, the optimum hydrogen to methane ratio was chosen as \(\text{H}_2:\text{Ar}:\text{CH}_4 = 20:400:50\).

6.4 METHODS AND CHARACTERISATION

Prior to growth, the tantalum foil was cut into 1 cm\(^2\) pieces, ultrasonically cleaned in acetone and isopropanol for 10 min and dried by compressed air. Tantalum samples were placed into a quartz boat introduced into a quartz tube at room temperature. After sealing the reactor and evacuating the growth chamber, the temperature was raised to 800°C - 1150°C depending on the particular experiment. It was found that the higher the temperature, the more surface changes can be observed on tantalum foil after the experiment (changes in colour, in surface roughness, and even in thickness). Although, in order to control the quality of grown carbon materials as well as the surface coverage, the growth pressure was very important. Thus, the optimal pressure in most experiments was around 150 - 200 Torr. Further pressure increase led to cracking the surface of tantalum foil and to amorphous carbon deposition. To clean and to smoothen the surface morphology the tantalum foil was annealed in vacuum / Ar (100 sccm) / Ar : H\(_2\) (100:10 sccm) atmosphere for 30 min. I did not find any differences between annealing environments. Next, after annealing, methane / methane and hydrogen was introduced into the growth chamber for 0.5 - 7 h, depending on the particular experiment. The desired working pressures in the
System were achieved by combining the stock gas mixtures \((\text{CH}_4: \text{H}_2 = 3:1\) in the case of low-pressure growth and \(\text{Ar} : \text{CH}_4 : \text{H}_2 = 5:3:1\) when pressure needed to be slightly higher). Then, the samples were held at the growth temperature for 1 - 5 h. After completion of the growth process, samples were fast cooled to room temperature in the same mixture but without methane.

In order to choose the optimum pressure and growth temperature, I performed graphene growth at different conditions. The results are summarised in Fig. 6.4.

The quality of graphene has been assessed by the Raman spectroscopy, Fig. 6.5. Our Raman spectra have been taken with a HORIBA Scientific XploRA PLUS Raman microscope using 532 nm laser source with a power of 15 mW and 10 s duration multiple exposures.

I found that reasonable quality graphene (with \(G/D\) and \(2D/D\) ratio being larger than 1) can be achieved only at high temperatures and medium pressures. Simultaneously, I also found that the growth of high-quality graphene is accompanied by the change in the morphology of tantalum foil, i.e. the colour of the surface gradually changes from metallic grey to yellow, Fig. 6.4a. Furthermore, the onset of the colour change precedes the growth of graphene.
To understand the growth mechanism, we look closely at the low-wavenumber part of the Raman spectrum. At low temperatures, only the tantalum oxide peak at 660 cm\(^{-1}\) can be seen, Fig. 6.5b. At higher temperatures, new peaks at 290 cm\(^{-1}\), 600 cm\(^{-1}\) and at 770 cm\(^{-1}\), which can be associated with tantalum carbide, start to dominate, Fig. 6.6. This suggests that the mechanism of graphene growth goes through the formation of tantalum carbide as a precursor for graphene. In our experiments, I found that Ta readily forms carbides already at 900°C, which can be easily recognisable simply by observing the colour change. It is evident that the foil is turned into tantalum carbide which is golden yellow (monocarbide TaC and hemicarbide Ta\(_2\)C\(^2\)). However, as seen from the enlarged image of yellow dot and Raman measurements around it, the TaC is not always related to the yellow colour.
Figure 6.6. Raman investigation the surface of Ta foil after the graphene growth. Numbers from (a) attributed to 1 - (b) - carbide, 2 - (c) - carbide + disordered graphene and 3 - (d) - high quality of graphene.

In order to prove this model that graphene growth takes place through the formation of carbide, I performed X-ray diffraction measurements. The microstructure analysis was performed using Rigaku SmartLab X-ray diffractometer with a standard copper anode sealed tube source with Tungsten filament, 40 kW 30 mA in a parallel beam mode. After graphene growth, the peaks which can be attributed to tantalum carbide\textsuperscript{213,214}, start to appear, Fig. 6.7d.
In order to check the thickness of the formed tantalum carbide, I analysed the cross-section (made by Focused Ion Beam) of the foil using scanning electron microscopy (SEM), Fig. 6.7.

Cross-sectional imaging and serial sectioning were produced by a hybrid FIB-SEM system Carl Zeiss Crossbeam 540. Oxford Instruments Silicon Drift Detector (SDD) X-max 80 in this system and AZtecEnergy EDS Microanalysis software were used for elemental analysis of the cross-section. ImageJ software was employed for three-dimensional (3D) image reconstruction. Simple SEM imaging and EDS analysis of the sample surface were performed using Carl Zeiss Ultra Plus SEM also fitted with Oxford Instruments X-max 80 SDD combined with AZtec software.

Both the brightness contrast and the elemental analysis allow clear identification of the tantalum carbide. The thickness of tantalum is approximately 400 nm for 1 h growth time using the optimal parameters (T = 1150°C, pressure 200 Torr). Thus, I can confirm that the growth mechanism of graphene on tantalum is different from those which occur on metals which do not form carbides: either through the precipitation mechanism for metals...
with high carbon solubility such as nickel\textsuperscript{216}, or through catalytic, self-limiting growth on the surface of metals with low carbon solubility, but with some catalytic activity towards cracking of hydrocarbons\textsuperscript{217}. In our case, under the exposure of the surface of oxidised tantalum to methane, the high catalytic activity of tantalum pentoxide lead to cracking of the methane and production of atomic carbon. Atomic carbon then dissociates through tantalum oxide and forms tantalum carbide. It also replaces oxygen and forms tantalum carbide at the surface (tantalum oxide becomes unstable against tantalum carbide if there is no supply of oxygen, but there is an excess of carbon\textsuperscript{218}). Finally, once tantalum carbide is formed, the excess carbon participates in the formation of the self-limiting graphene layer. The thickness of the carbide layer is determined by the kinetic conditions and represents the balance between the speed of carbon diffusion into tantalum and graphene formation/etching on the surface. It is important to note that the detailed mechanism requires further investigation.

6.5 Corrosion tests

Both graphene and tantalum carbide are considered to be efficient corrosion protection layers\textsuperscript{8,42,219}. I performed two types of corrosion tests: exposure to corrosive liquids and high-temperature oxidation. Since carbides can protect against corrosion alone, I first checked the role of graphene in chemical corrosion test (Fig. 6.8). The sample with full surface coverage by carbide and graphene was cut into two pieces. One of the pieces underwent oxygen-plasma treatment for 2 min to etch away the graphene layer. I used soft oxygen/argon plasma during such a short period of time, so that carbide layer remained intact. Then both pieces were tested for the corrosion in 30% NaOH. The results of the test are presented in Fig. 6.8.
Figure 6.8. Photographs and optical images of tantalum foil showing results of chemical corrosion test (20 h treatment in an aqueous solution of 30% NaOH at 70 °C). Panels (a - f) are the photographs and optical images before the corrosion test, panels (g - l) after. (a) Photograph of pristine Ta foil, (b) Ta foil from which graphene was etched in an oxygen plasma, (c) Ta with protective graphene layer, panels (d - f) show corresponding optical micrographs for panels (a - c). Images on panels (g - l) are the same as on (a - f) but taken after the corrosion test. All scale bars for (d - f) are 50 µm and for (j - l) are 100 µm. Image from.\textsuperscript{200}

After the growth process, the grey surface of tantalum turns yellow because of interference contrast due to the small thickness of the protective layer (Fig. 6.8a and c). The surface of pristine tantalum foil after the chemical treatment shows a deep penetration of NaOH inside the foil (Fig. 6.8j), while the surface protected with graphene foil (Fig. 6.8i) did not show any visible changes. On the Ta foil sample, where graphene was etched away, the lack of
protection from alkali solution was observed both by an optical microscope and by the naked eye (Fig. 6.8h and k). Before and after the corrosion test the Raman spectra of tantalum surface were taken for samples on panels b, c, h, i of Fig. 4. Therefore, strong etching of the surface (of both of the native oxide and the tantalum itself) occurs on the unprotected sample. For the sample protected with carbide and graphene, no etching has been observed, and graphene was found to be present on the surface after the procedure.

Figure 6.9. Raman spectra of the sample from Fig. 6.8 Panel (a) - spectra of the sample with graphene (left) and the sample where graphene was etched away (right) before the corrosion test. Panel (b) – Raman spectra of the corresponding samples after the 20 hours of corrosion test. After the test, the distinct graphene peaks (D, G, 2D) still can be found (b, left), revealing that graphene can survive the severe alkaline treatment. The results of chemical corrosion test vividly demonstrate the protective properties of carbide/graphene layers. Image from.200

In order to check the oxidation resistance of our samples, I exposed them to an oxygen atmosphere at ambient pressure and elevated temperatures, Fig. 6.10.
It was found that prolonged exposure of untreated Ta to oxygen leads to the formation of a thick layer of white tantalum oxide even at 350°C. At the same time, tantalum carbide and graphene protect tantalum very efficiently even at temperatures above 650°C. However, I should mention here that graphene alone is efficient as antioxidation barrier only at temperatures below 300°C. At higher temperatures, it burns in oxygen atmosphere within a few minutes.
In order to check the number of layers, I transferred our CVD-grown graphene from Ta foil to a silicon wafer (290 nm SiO$_2$ on Si) using bubble transfer method described elsewhere\textsuperscript{50}. After that, I performed AFM topography and Raman mapping measurements confirming that the thickness of the graphene layer is indeed a monolayer.

Figure 6.11. Raman mapping of CVD graphene grown on Ta foil and transferred on SiO$_2$/Si substrate. (a) optical image of the mapped area (20x14 µm), (b) Raman map of D-peak area, and (c) Raman map of the 2D/G ratio. The results demonstrate that graphene grows mostly as a monolayer and bilayer on Ta foil. Image from\textsuperscript{200}.
Figure 6.12. The optical image (left) and AFM pictures (right) of scanned areas of CVD graphene on SiO$_2$. The thickness of graphene at the edge (1) and at the folded site (4) is 4-6 nm, in the middle sites (2, 3) it is 1-2 nm, which means that graphene is mostly mono- or bilayer. Image from.$^{200}$

Figure 6.13 shows optical micrograph of transferred graphene, large continuous areas of monolayer graphene are clearly visible; Raman spectra confirm that graphene is indeed a monolayer. From the transferred graphene a multi-terminal transistor device was fabricated using a standard e-beam lithography followed by e-beam metallization of 5 nm Ti and 80 nm Au (device micrograph is shown in the inset in Fig. 6c). Resistivity follows typical for graphene peak-shaped curve$^{67}$ with the neutrality (Dirac) point around -10 V, indicating slight n-type doping, possibly due to the presence of polymer residues and impurities in the SiO$_2$ layer.
Figure 6.13. CVD-grown graphene transferred from tantalum foil to SiO$_2$/Si wafer. (a) Optical micrograph, (b) Raman spectrum of the marked spot, and (c) the resistance of graphene device as a function of gate voltage. Raman spectrum corresponds to a monolayer of graphene. The D-peak is more intense as compared to that obtained before the graphene transfer. The increase in the D-peak intensity can be related to the wet transfer during which more defects appear. Strong field effect behaviour confirms the high quality and the atomic thickness of the transferred graphene. Image from.$^{200}$

6.6 CONCLUSIONS

In conclusion, graphene growth on tantalum occurs via the initial formation of carbide, which acts as a catalytic surface for the graphene deposition. Such combination of graphene and carbide forms very efficient corrosion and oxidation protection barrier, which can be used in the production of desired radioisotopes through nuclear reactions with high cross-section by the interaction of a proton beam with the target thick materials$^{220}$. 
7. CVD OF GRAPHENE ON RHENIUM

This work was carried without any collaboration; all parts of the work were made by myself.

7.1 INTRODUCTION

7.1.1 Interaction of rhenium with carbon

Rhenium (Re) was chosen as a target metal to grow anticorrosion graphene layer because according to works\textsuperscript{221,222}, it was proposed as the transition metal (TM) which does not form carbides while reacting with carbon. This fact was quite attractive in sight of my previous work with tantalum, where the growth of graphene was accompanied by a carbide formation. Carbides are not desirable materials because of the exceeded (additional) amount of carbon in bulk metal decreases the yield of useful radioisotopes after proton irradiation\textsuperscript{223} for medical applications\textsuperscript{1}. Therefore, it was important to find out what is known in the literature about Re-C interactions and whether Re carbides exist or not.

First of all, it is worth to reminding here that carbon - metal interactions and forms of carbon obtained, depend not only on conditions at which the process of interaction occurs, i.e. pressure and temperature, but rather governed by the fundamental intrinsic properties of metal - its external electron configuration\textsuperscript{94}.

TM can react with carbon with various degree of intensity by overlapping its d-orbitals with carbon p-orbitals. This ability appears to increase with the increasing number of electron vacancies in the d-orbital, dividing TMs into three general subgroups with low (Cu, Au), moderate (Fe, Co) and strong (Ti, V) interaction with carbon. The increasing reactivity between metal and carbon also reflects in the increasing solubility of carbon in metal. However, this trend reaches its peak at iron group metals and then declines. That happens due to overreaction between metal and carbon, as after certain threshold value of reactivity, carbon atoms begin to lose their mobility in solution and eventually locked up in the metal structure as a carbide\textsuperscript{94}.

Re, having the \([\text{Xe}5d^56s^2]\) electron configuration, lies in the metal group that actively reacts with carbon. Despite the high carbon solubility and the intermediate occupancy of the d-orbital, Re is not a carbide-forming metal. (Re is considered to be not a carbide-forming metal despite having high carbon solubility and its intermediate occupancy of the d-orbital).

Its electron configuration makes it similar to Mn and Cr in terms of interaction with carbon. Next, Re is an element of group VII of the periodic table, and it has similar physical
properties to group VI metals, i.e. Mo and W\textsuperscript{224}. On the other hand, it exhibits characteristics
typical for platinum group metals (Pt, Ru, Os). Further investigation of literature regarding
rhenium – carbon interaction led to more confusion and still remains quite unclear and full
of ambiguities.

In the earlier work\textsuperscript{225} authors reported no reaction between Re and carbon and no
agreement was whether a stable carbide exists or not. Moreover, until the mid of the 20\textsuperscript{th}
century, it was believed that Re does not form carbides, that carbon solubility in Re is
extremely low and that carbon-Re interactions are rather weak\textsuperscript{226}. Later, in some works
authors reported that carburization effect is influenced by the type of carbon gas source
and the form of Re samples (e.g. foil, powder, etc). Thus, it was reported\textsuperscript{227} that Re carbide can
be formed when rhenium powder was exposed to carbon monoxide. In work\textsuperscript{228}, authors
prepared rhenium-carbon alloy by melting small compacts of rhenium powder and graphite
in argon. They found that the equilibrium phase diagram of Re-C liquid is very similar in form
to the cobalt-carbon and the nickel-carbon systems. The solubility of carbon in Re is rather
high and can reach 16.9 at% carbon (at 2480°C). After cooling the Re-C alloy, some graphite
flakes were found on Re surface; also in this work, it was concluded that no Re carbide
existed.

Carbon solubility in metal is, indeed, a temperature-dependent process. When talking about
the solubility of carbon in Cu, for example, the mentioned temperature in most reports is
1000°C. For Cu, this temperature is very close to the melting point, although carbon
solubility remains still very low even at 1080 °C – 0.04 at%\textsuperscript{229}. Information about the
solubility of carbon in rhenium varies in different works, but in general, everyone agrees that
it is quite high. In the work\textsuperscript{94} it was reported to be 4.39 at% 1000°C although in the work\textsuperscript{230} it
was estimated to be 0.35 at% at the same temperature, which is still quite high.

Also, it was proposed that carbon solubility in Re has a limit. The solubility limit of carbon in
Re was found by the exposure of the heated metal to benzene vapours\textsuperscript{231}. Benzene
dissociates on the surface of hot metal, hydrogen desorbs, and the carbon remains on the
surface or dissolves in the rhenium bulk. Thermal desorption of carbon was observed only at
T > 2100 K, indicating Re - C equilibrium range. Authors explicitly studied the “solubility
limit”, and they reported that carbon solubility in Re is temperature-dependent starting
from 1.25 at% at 1600K (1300°C) and reaching its maximum by 3.25 at% at 2050 K (1650 °C);
after that carbon starts to desorb from the surface. This temperature range is reported in
terms of graphene island nucleation/dissolution on/from the surface.
In the 1970 Popova et al.\textsuperscript{232} claimed that ReC was synthesised under high pressure (16-18 GPa) and high temperature (1273 K). The phase diagram of the Re-C system shows that there is no stable Re-C compound formed under ambient pressure. Also, in the literature there are few reports concerning the existence of Re carbides within pressure range 10-67 GPa and temperature range 1273-3800 K\textsuperscript{232-234}. In some works the existence of Re carbides was proposed based on theoretical calculations only\textsuperscript{235}.

In the relatively recent work\textsuperscript{236}, it has been reported about a hard ultra-incompressible bulk Re\textsubscript{2}C material which was synthesised under moderate pressure (2-6 GPa) and high temperature (873-1873 K). Therefore, high pressure and temperature seem to be prerequisites to obtain rhenium carbides.

In the group of scientists headed by Gall, many works dedicated to the investigation of carbon-TM interplay were produced. Their works originate from the 80s\textsuperscript{237} of the last century, and until now the carbon-Re system is currently enjoying the strong attention of the mentioned research group\textsuperscript{238}. Among many Me-C systems they studied (Ir, Mo, Ni, Rh, Pt), Re-C system is found to be the most convenient in terms of growth of graphene layers in a controllable way (as they claim).

From one work to another, the method used in the Gall’s group is the same with the slightly shifted focus on different aspects of the mechanism of the process. They performed experiments in UHV (10\textsuperscript{-10} Torr) Auger spectrometer where Re sample was carbonised in benzene vapour atmosphere with the partial pressure of benzene 10\textsuperscript{-5} Torr. Also, this ultra-high vacuum apparatus is coupled with an additional module for surface diagnostics to determine the relative area of graphene. In work\textsuperscript{239} they raised the temperature to the maximum possible values (~2000 K) and then decreased it stepwise. They found that carbon undergoes several steps during temperature change. At the highest temperature only chemisorbed carbon was found on Re surface in the form of “dense carbon gas”. When the temperature starts to decrease to 1390 K, graphene islands start to grow; carbon, which was dissolved into the bulk, thanks to “high and noticeable carbon solubility in Re”, starts to diffuse to the surface and forms first graphene islands leading to the continuous graphene layer. Further temperature decrease led to the formation of the second layer, and so on.

The limiting stage of graphite growth on Re surface is the diffusion of carbon atoms over the metal bulk towards to surface. In their study\textsuperscript{231} the temperature range for precipitation of carbon from Re bulk to its surface was investigated which was 1200-1600°C and this range was found to be much narrower as compared to other metals they worked with. Described
bottom-up mechanism of the formation of graphene layers on Re surface is reversible as they observed backwards process with increasing temperature after the graphite formation, i.e. dissolution of graphene and observation, again, of only chemisorbed carbon on the surface\textsuperscript{229}.

It is also worth noting that the work of that group did not report on the formation of any (bulk or surface) Re carbides. Signals from Auger spectrometer attributed to carbide shape were observed when worked with Ni and Mo, but not with Re\textsuperscript{240}.

Apart from the works of Gall’s group, information concerning the growth of graphene on rhenium is limited to occasional publications.

Miniussi et al.\textsuperscript{222} investigated the corrugation in epitaxial graphene grown on Re (0001) and its relationship with the thermal stability. The experiments were carried out at Nanospectroscopy beamlines of the Elettra synchrotron radiation facility. They grew epitaxial graphene on Re single crystal via CVD, by repeatedly heating up the crystal to 1090 K in a C\textsubscript{2}H\textsubscript{4} background with working pressure 5x10\textsuperscript{-7} mbar. The results, based on the combination of photoelectron spectroscopy and density functional theory (DFT) calculations, concluded that graphene on Re (0001) starts to break up just above 1000 K which they explained by strong corrugation of graphene and Re surface. Also, they reported that there is a close relationship between graphene corrugation and its thermal stability, which is a key achievement in sight of the potential high-temperature applications or as a protective layer under highly oxidising conditions of supported graphene. In that work, authors also highlighted the fact that Re is not a carbide forming metal.

Later, the same authors\textsuperscript{241} reported a different approach to the growth of graphene on Re (0001). They exposed the Re (0001) substrate to C\textsubscript{2}H\textsubscript{4} and subsequently annealed the sample to a higher temperature. At T > 750 K, the thermal decomposition of C\textsubscript{2}H\textsubscript{4} on Re (0001) results in a competitive interplay among three processes: graphene growth, surface carbide formation, and carbon bulk dissolution. They observed that graphene/Re(0001) is not stable at 1000 K (= 700°C). Above this temperature the depletion of the carbon layer was observed, accompanied by a simultaneous appearance of surface carbides, whose formation is in turn opposed by carbon bulk dissolution. Finally, no surface carbides were found at temperatures higher than 1350 K. Therefore, the results of this work are consistent with those of Gall’s group which also reported on different carbon forms on Re surface depending on the temperature, although, no reports about carbides. The most intriguing work was conducted by research group\textsuperscript{242}, where they also showed the growth and transformation processes
from graphene to carbide on Re (0001). Graphene on Re surface was synthesised by exposing Re (0001) to ethylene in UHV, $5 \times 10^{-9}$ mbar. They conducted three different processes: (i) Exposure of Re single crystal to ethylene at ≈903 K led to the formation of only graphene. (ii) When the same process was repeated at 1113 K, and the sample was cooled down, a layer of Re carbide was detected, and (iii) when the clean substrate (without carbon precursor) was annealed at 1113 K, the Re surface also was covered by carbide! The results of the last process indicate that Re has a great affinity to carbon and show that carbon solubility in Re is not zero even at room temperature. Nevertheless, this fact was left without proper attention by authors. The similar phenomena concerning the low-temperature solubility were mentioned in work\textsuperscript{241}, when it was reported that C\textsubscript{2}H\textsubscript{4} undergoes a dehydrogenation on Re surface already at ≈300 K. And again, there were no any discussions, they just concluded that this is in agreement with earlier work by Ducros et al.\textsuperscript{243}

Apart from this interesting fact about carbon solubility in Re at room temperature, the reported results on the transformation of graphene to carbide with increasing the temperature are opposite to the effect in Ni. For instance, in the work\textsuperscript{244} the conversion from Ni\textsubscript{2}C to graphene by surface carbon in-plane migration from carbide to graphene was reported. Besides the diverse transformations, in the case of work by Chinese researchers, carbide was not formed at the edges of graphene domains but distributed randomly on the substrate surface. The temperature window at which graphene can be formed/dissolved on Re (0001) they reported was 903-983 K.

In the work\textsuperscript{245}, the authors investigated the effects induced in the electronic structure of monolayer graphene, epitaxially grown on SiC (0001), after Re deposition and subsequent annealing. As they reported, Re was chosen as a good candidate among all the other refractory metals as a non-carbide forming one. Therefore, even in the recent articles, there is no solid opinion about the existence of Re carbides. Perhaps, high pressure and temperature are necessary conditions for bulk carbide formation\textsuperscript{233}. For the formation of surface carbides, the moderate temperature and pressure close to UHV are enough, which is at least weird effect, though\textsuperscript{242}.

Also, the role of a low pressure which was applied in all works of graphene deposition on Re was not explained. Only in the work\textsuperscript{241} the authors tried to explain the application of low pressure to avoid the simultaneous formation of multiple nucleation centres on the substrate surface.
Therefore, after taking into account the results of mentioned above works, there is no solid conclusion about the existence of Re carbides as well as no accurate temperature range for graphene growth on Re single crystals and especially on polycrystalline Re.

### 7.1.2 Catalytic activity of rhenium

Re was reported to be a great catalyst for the growth of single- and multi-walled CNT\(^\text{246-248}\). Efforts were also made to decorate graphene with Re occurring in the form of ultra-small rhenium clusters consisting of 2-13 atoms of Re\(^\text{249}\).

In many works, it was shown that decomposition of hydrocarbons occurs preferentially on some crystal faces of rhenium, namely on (0001)\(^\text{222,241,242,250,251}\) and on (0101)\(^\text{252}\) faces. The catalytic activity of polycrystalline Re is shown to be anisotropic\(^\text{253}\). In the case of Re surface with various faces\(^\text{240}\), the rates of carbon dissolution, as well as the mechanisms of carbon-structure formation upon cooling, in various regions, can be different. This can lead to the formation of carbon structures with various phase compositions — from graphene islands in some phases to the graphite phase in other surface regions.

There are also studies where graphene served as a template to grow Re-containing structures. For instance, in the work\(^\text{254}\) the epitaxial growth of monolayer Re\(_2\)S (another member of the family of 2D transition metal dichalcogenides) on CVD-grown graphene was investigated. The smooth and inert graphene surface allowed to grow monolayer of Re\(_2\)S where most of the domains of Re\(_2\)S were crystallographically aligned to the graphene substrate orientation.

### 7.2 Growth process

In this work, the Re foil from Goodfellow Ltd. with a thickness of 0.2 mm was used. The different approaches to grow graphene on Re foil were applied. I did not use the isothermal-isobar method like with Ta since it is known from the literature that pressure close to UHV is applicable to Re-C system during the graphene growth. However, to be sure that for Re a quite narrow window of growth conditions is applicable, experiments with relatively low temperatures and high pressures were conducted as well. The results will be discussed below. The following variations in growth parameters were used:

- Temperature range: 950-1200°C
- Pressure: 2-3 Torr-100 Torr
- CH\(_4\)/H\(_2\) range: 10/20 - 100/200 sccm
- Growth time: 1h - 7h
- Cooling fast/slow rate – 2h/10h.
Below we consider the influence of some of the parameters on the resulting graphene deposition on Re foil.

### 7.2.1 Surface pre-treatment

As received the surface of Re foil was covered by impurities, looked inhomogeneous and quite dirty. The first problem was the preparation of the clean surface. For rhenium, this turned out to be remarkably easy to do. Before the growth, Re foil was cleaned in acetone–isopropanol–deionised water and dried in compressed air. Fig. 7.1 presents optical and SEM images of Re foil surface before (a), (c) and after annealing (b), (d) in a hydrogen atmosphere for 30 min at 1000°C.

![Figure 7.1](image.png)

**Figure 7.1.** Optical (upper) and SEM (bottom) images of Re foil surface before (a), (c) and after (b), (d) annealing.

The Re foil was inhomogeneous in colour comprising different dark and white areas - the SEM/EDX analysis revealed the presence of impurities in the form of surface oxides. SEM
analysis of the surface of rhenium is more representative than just optical microscope investigation and revealed the influence of annealing more visibly.

On the panel (c) of Fig. 7.1 one can see the impurity particles and clusters of different shapes. Hydrogen annealing significantly improved the appearance of Re surface panel (d). It is clear that the surface of the foil becomes more homogeneous, panel (b), dark regions become less visible, even disappeared. Like in the case with Cu, a hydrogen reducing environment enables the removal of the oxide layer and other surface impurities. Etching effect of hydrogen on amorphous carbon and surface oxides were reported elsewhere. SEM analysis also revealed that this procedure removed all traces of surface impurities.

7.2.2 Influence of prolonged annealing

Interestingly, annealing at higher temperature and pressure led to unusual surface recrystallisation. Figure 7.2 presents SEM images of Re foil taken after prolonged (up to 2 hours) annealing in H₂+Ar at different temperatures.

![SEM images of Re foil](image)

Figure 7.2. Influence of the prolonged annealing at high pressures and temperatures.

Re is well known because of its thermal stability and high melting point (3182°C). Also, according to the study, the reactivity Re with hydrogen is very low – there are no Re hydrides reported. In the work, though the first experimental evidence for neutral rhenium hydride molecules was reported which were obtained at the low-temperature (at 3.5 K). Nevertheless, with an increase in the annealing temperature, Re surface has changed, became softer, and the appeared waves indicated the pre-melting state of the subsurface
layers. Similar picture as on panel with 1100 °C in Fig. 7.2, showing waves on the surface, often is observed during Cu annealing\(^{258}\) at a temperature close to Cu melting point. In contrast with Cu, where prolonged hydrogen reduction pre-treatment enlarges the grain size, in the case of Re, the opposite effect was observed. Fig. 7.2 panel with 1150 °C clearly shows that polycrystallinity of Re foil is drastically increased. The reason why annealing led to such a surface reorganisation might be the relatively high pressure applied, the total pressure of the system was > 60 Torr. Although a similar effect of recrystallisation of Re surface was reported\(^{255}\), where Re thin ribbons underwent cleaning at 2200K in 10\(^{-6}\) Torr by oxygen – thus, neither the pressure nor the environment are the reasons.

Therefore, to avoid the increase in polycrystallinity, the annealing in a vacuum and then in hydrogen only at 1000 °C (keeping the pressure not higher than 10\(^{-1}\) mbar) were selected to conduct prior every growth.

First of all, the usefulness of applied SEM characterisation should be presented. Fig. 7.3 shows the imaging using different SEM detectors – note the difference between the images obtained with a secondary electron (SE) and InLens detectors of SEM. The signal of SE detector does not clearly reveal the location of the graphene islands; there are some areas with slightly different contrast of the surface, whereas the InLens detector shows locations of graphene islands clearly and accurately, the contrast with the uncovered surface is very clear – darker areas are graphene islands on the surface. Figure 7.3 illustrates the difference between detectors: images of the same spot 1 (a), (b) and the edge of the Re foil 2 (c), (d).
7.2.3 Non-uniform deposition of graphene

As it was described above, graphene grows on Re surface preferentially on (0001) face\textsuperscript{222,242}, therefore it was not a surprise that graphene was found on the foil after growth in forms of islands and spots, but never covered the Re surface completely. In contrast to the Cu foil, where graphene layers and islands are clearly seen through the optical microscope\textsuperscript{45} (mostly because of wrinkles), in the case of Re, only at high magnification was it possible to find some regions which, by colour, slightly differ from the bare Re surface. As seen from the optical images and SEM (Fig. 7.4) the graphene islands start to nucleate and grow from cracks, grain boundaries and residual impurities on the surface. With an increase in the reaction time, the graphene islands become more visible due to the increased thickness, Fig. 7.4b. As it was mentioned above, a picture captured with SEM,
particularly using InLens detector, is clearer and the contrast with the Re surface is higher. One of the islands from panel (b) was investigated by SEM – panel (c), Fig. 7.4.

![Graphene islands](image)

**Figure 7.4.** Influence of the prolonged growth time on the deposition of graphene on Re surface.

It is clearly seen that graphene distributed highly unevenly. The reason for that might be the polycrystallinity and therefore the high anisotropy of Re surface. There are distinct islands of graphene which were not expanded during the growth process but rather increased in thickness. Therefore, a higher number of layers represented by darker regions. Besides the islands, there are black spots around the islands. Notably, these dark spots are not seen through the optical microscope, but being captured by SEM and analysed by Raman, spots and regions adjacent to islands are defective graphene, amorphous carbon (AC) and soot.

### 7.2.4 Influence of methane and prolonged reaction time

It was found experimentally that gases ratio was ideal for graphene growth. Increasing the partial pressure of methane and reaction time led to a very similar effect on results - the formation of denser deposition of AC – Fig. 7.5.
With the hope to increase the graphene coverage of Re surface, the growth process was prolonged. The longest time experiment conducted was overnight (up to 7 hours). Again, increasing the methane flow exposure to the Re surface did not increase the coverage significantly. More small islands appeared, but the previous did not become larger. That might be attributed to the increased total growth pressure of the system. Further increase in growth time was not conducted since the duration of 7 hours is already showed that the kinetic factor is not limiting (decisive) in this process. Perhaps, the total coverage could be reached eventually, but the further increase in growth time would be associated with the appearance of undesirable deposition of amorphous carbon. In other words, carbon preferentially deposited on existing islands rather than extended them.

### 7.2.5 Influence of temperature

A range of reaction temperatures was applied, varying between 900°C and 1200°C. Then I tried to grow graphene at relatively low temperatures (the lowest temperature was 900°C), but no graphene islands were found, just invisible via optical microscope amorphous carbon. Raman investigation of the surface after low-temperature growth revealed mostly peaks at 1300 cm⁻¹ and 1600 cm⁻¹ without a 2D peak at 2700 cm⁻¹. The first graphene islands on Re foil start to nucleate from temperature 1050 °C, a further increase in the temperature led to the formation of more new islands but still very small ones. At temperature 1120°C the
surface coverage became larger, and the islands merged, although the thickness of already existing islands increased and the coverage was never complete.

Further temperature increase started to change surface significantly, e.g. at 1200°C graphene islands did not appear, indicating that all carbon was dissolved into Re bulk and for the graphene deposition on Re there is just a narrow window of conditions. Thus, my results are in good agreement with reported results\textsuperscript{241} with the only difference in the temperature range.

Fig. 7.6 shows optical image and Raman spectra of the different areas of deposited graphene on the Re surface after the growth at 1100°C. Raman spectra can be attributed to mono-, bi-, and a few-layer graphene. In general, lighter colours were associated with thinner FLG and darker ones to thicker FLG.

Such phenomena of non-uniformly grown graphene on Re might be attributed to general catalytic anisotropy of Re surface and therefore could partly explain the inhomogeneity of carbon deposition on the surface. Perhaps, claimed catalytic activity of Re\textsuperscript{247} is only applied to Re single crystal surface with (0001) crystal orientation since even cleaned from impurities, the annealed surface shows a low performance for graphene formation.
7.2.6 Influence of pressure and hydrogen

In order to reach the conditions close to a high vacuum as suggested in the literature, the turbo molecular pump was connected to the CVD reactor, and the system was pumped down to $10^{-5}$ mbar which was the lowest vacuum I could achieve. As it was mentioned above, the increase in growth pressure led to the formation of only AC.

There was no visible difference observed in resulting graphene deposition depending on high or low hydrogen impact during the growth process. Variations in hydrogen impact were conducted keeping the input of methane constant. Therefore, the only role of hydrogen was cleaning/annealing of the Re foil surface prior to the growth.

7.3 **Possible mechanism of graphene growth on Re foil**

The fact that Re, despite its great affinity to carbon, forms graphene differently as compared to Ni, can be proven by the following experiment.

Fig. 7.7 presents the micrographs of the surface of Re foil after the growth of graphene at 1170 °C followed by the slow cooling. One can clearly see the large and contrasted black regions – soot deposition, as revealed by Raman analysis.

![Figure 7.7. Optical (right) and SEM (left) images of Re surface after the growth at 1170 °C](image-url)
The left panel shows that deposition of carbon started from grain boundaries; the large black spot of amorphous carbon and some uncovered (grey colour) areas indicate that Re foil remains anisotropic even for carbon deposition from bottom up.

Interestingly, the deposition took place during the cooling when methane was switched off, i.e. no external carbon was introduced into the reaction chamber, and the only possible source of carbon was the bulk of the Re foil. The similar process of segregation of dissolved carbon towards to the surface during the cooling was reported\textsuperscript{242}. The difference was that in that work, the study object was Re single crystal and they found Re carbides on the surfaces which formed during the cooling step. They reported that such a segregated growth mechanism of rhenium carbide is a newly discovered characteristic of Re (0001).

### 7.4 Carbide formation on Re surface

As it was described in the literature survey above, the formation and existence of Re carbide remain a huge uncertainty. In our work, no evidence of Re carbide was found – XRD spectra of Re surface were taken after several processes including (i) the annealing of Re foil in hydrogen, (ii) the growth of graphene at different conditions, (iii) slow cooling with soot deposition. In addition, after the growth processes at different conditions, Raman investigations were made. Fig. 7.8 shows XRD spectra (insert shows Raman spectrum) of Re foil after the graphene growth under the following conditions: temperature/pressure/gases ratio/growth time – 1050°C/50 Torr/1:2/1 hour. The XRD pattern has a distinct peak with high intensity attributed to Re only. No peaks corresponding to carbides were found\textsuperscript{233,236}. Similar patterns were found in all aforementioned experiments. Raman spectra with extended range were taken to make sure that no surface Re carbides formed. According to the work\textsuperscript{259}, the Raman peaks corresponding to ReC should have appeared at ≈125, ≈175, and ≈280 cm\textsuperscript{-1}.  

Therefore, I could conclude that Re does not form carbides and I join the supporters of this statement, but I believe that only certain conditions (which was never applied in my work) can provide the formation of Re carbides.

7.5 **Corrosion Tests**

7.5.1 **Acid corrosion**

As previously mentioned, Re itself is highly resistant to aggressive chemicals bar the concentrated nitric acid. Thus, it was decided to perform the corrosion tests by immersing Re foil after the graphene growth in acid media. The experiments were carried out in 50% nitric acid at room temperature. For this corrosion test, the samples of Re foil with maximal graphene surface coverage were chosen. Untreated, bare Re foil was used in the same procedure as a blank.
Figure 7.9 presents Re foil after the corrosion test for 30 min in 50% nitric acid. On the left panel Re protected by graphene islands is presented, on the right panel – bare Re foil.

The test results clearly show the protective role of deposited graphene. Bare Re foil was deeply corroded in acidic media even in 30 min of immersing, whereas foil covered by carbon products shows slower corrosion rate. For carbon-protected Re foil the picture comparable to that bare Re experiment was observed only after 6 hours of nitric acid treatment. In white areas where the density of graphene islands was larger as compared to the darker regions, the oxidation was minimal. In darker regions where graphene did not cover the metal surface uniformly, the surface was partly covered with a single layer of defective graphene which can be easily detached, and oxidation at these sites was the highest.

Figure 7.10 shows SEM images of a graphene island survived after 1 hour of acid treatment (left panel) and after 3 hours (right panel). On the right panel, it is obvious that the etching went deeper and only a small spot of graphene remains on Re surface surrounded by a deeply etched Re.

According to the work of Gall’s group dedicated to the investigation of intercalation of sodium atoms into thin multilayer graphene and graphite films on rhenium\(^{260}\), the first graphene layer plays the role of a trap to which atoms coming to the surface diffuse through a graphite film. The degradation of graphene layers under Na intercalation on the metal surfaces occurs layer by layer. The fact of layer-by-layer etching is in contrast with the following work\(^{261}\), where the authors investigated how graphene is removed from Ru(0001)
by reaction with oxygen. They etched graphene island on Ru (0001) via exposure to $6 \times 10^8$ Torr of oxygen at 550 K. This process involved intercalated oxygen, which destabilises graphene resulting in the etching of graphene edges. It was presented that both layers of the bilayer islands are etched together. Wrinkled regions where graphene detached from the substrate were found to oxidise substantially faster than flat graphene regions.

Figure 7.10. SEM images of residual of graphene on a deeply etched Re foil. Left – after 1 hour and right – after 3 hours in 50% nitric acid.

On the left panel of Fig. 7.10 one can notice that the etching of graphene layers is occurring from the edges, but all layers are etched simultaneously.

Graphene and dissolved into bulk carbon keep the rhenium and rhenium oxide together and cease any losses of the material while unprotected rhenium starts to lose mass; nitric acid penetrates all the way completely into the material. Beneficially, even if the metal becomes highly destructed by oxidation, the graphene layers help to keep the structure together and to eliminate material release into the environment.

The acid corrosion test was also conducted on Re foil covered with transferred from Cu CVD-grown graphene. After such a procedure, the corrosion test revealed no substantial difference between covered and uncovered Re foil. The reason might be in the bad contact of transferred graphene with the substrate foil since epitaxial growth (or direct growth on the metal substrate) provide better adhesion and, therefore, better protection.

On the SEM images obtained after etching rhenium foil in nitric acid, black spots show better protection provided by multilayers of graphene. In contrast, regions of unprotected Re
surface show a rough surface structure and are much more blurry; likely due to a charging effect from the presence of oxides.

7.5.2 Temperature corrosion

The Re foil sample with one distinct graphene island was taken to conduct the temperature corrosion test. The sample was heated on a hot plate at 250°C for 3 hours to check the resistance of the deposited graphene to oxygen at relatively high temperature. The test results are presented in Figure 7.11.

Raman investigation of a certain spot on the graphene island and the regions adjacent to this island were taken before and after the test. It is clearly seen from the images that heating in the air affected the area around the island. Before the test, Raman spectra of the surrounding area showed the presence of defective graphene - all representative graphene peaks were found, though, the signals were of quite low intensity (inset in Fig. 7.11b). Then Raman analysis was repeated after the test – panel d. Spots for the Raman investigation were taken as close as possible to the original ones. As one can see the temperature oxidation of Re surface changed the quality of the graphene Island – from perfect monolayer with negligible defects (small D peak on panel b) graphene became more disordered, intensities and shapes of the main peaks indicate lower quality of graphene (panel d). As for the regions of defective graphene around the island, no trace of any distinctive Raman peak was found after the test, not even for AC. Inset in Fig. 7.11d shows Raman background “noise” which is very similar to that of bare Re foil. From this test one can conclude that only highly structured graphene (mono-, bi- and multi-) can survive high-temperature oxidation with some surface reorganisations indeed, but defective graphene converts to amorphous carbon, which in turn burns in the air leaving the Re foil unprotected.
Figure 7.11. Optical images and corresponding Raman spectra of graphene island on Re surface (a and b) – before and (c and d) – after the oxidation of foil in air.

As the previous test with nitric acid, this one revealed the protective properties of graphene. The first anticorrosion properties of graphene were demonstrated in the work\(^{41}\), where graphene films grown by CVD were shown to protect the surface of the metallic growth substrates (Cu and Cu/Ni alloys) from oxidation, both in the air at elevated temperatures, as well as in hydrogen peroxide.

The observed effect of corrosion protection is believed to originate from the graphene’s impermeability to the liquids and gasses, which leads to insulating the underlying material from exposure to corrosive species. The full potential of graphene as a protective layer can be understood based on its unique physical and chemical properties. First, surfaces of sp\(^2\) carbon allotropes form a natural diffusion barrier, thus providing a physical separation between the protected metal and reactants.

Second, graphene has exceptional thermal and chemical stability. Combined, these two properties (impermeability and thermal/chemical stability) alone would make graphene an excellent candidate for a novel protective layer.
7.5.3 Crystal structure of studied transition metals

One of the important issues of CVD grown graphene on polycrystalline foils is a random orientation of growing crystals. There are two growth orientations which can be defined depending on graphene edges: armchair and zigzag (Fig. 7.12). When graphene starts to nucleate and grows on metal surface developing in bigger flakes (domains), the density of grain boundaries depends on crystal size and its orientation. The boundary of graphene domains can be seamlessly aligned in case of the same orientation of neighbouring domains. When the orientations of domains are random, graphene domains are misaligned with respect to the neighbouring domains. The random orientation of graphene domain edges results in many defects in the form of rough stitches. The high density of grain boundaries in graphene affects not only the low transport mobility but influences on the anti-corrosion performance\textsuperscript{262}.

Figure 7.12. Graphene lattice with zigzag and armchair edges. Image adapted from\textsuperscript{263}.
In order to avoid the energetically unfavourable graphene boundary formation, graphene predominantly grows on sites with (0001) faces of rhenium polycrystalline foil and Cu foil with (111) faces\textsuperscript{222,264}.

Metals with hexagonal closed packed structure (hcp) (0001) or face-centred cubic (fcc) (111) planes symmetry matches with the graphene structure. Therefore the epitaxial growth of graphene on mentioned crystallographic planes is preferential.

Both fcc and hcc are close-packed structures. Atoms are in close-packed planes, but with different stacking order.
In case of the growth of graphene on tantalum, the polycrystallinity of the foil did not play an important role since the deposition of graphene occurred through the carbide formation and graphene did not attach to the metal surface directly.

### 7.6 CONCLUSIONS

1. Despite the high carbon solubility in Re, mechanism of graphene formation is different from that on Ni. The process of graphene deposition on Re surface might occur through both catalytic dehydrogenation and segregation from the bulk.

2. Our results are consistent with opinion from the literature that graphene on Re surface can exist only in a certain window of conditions, especially temperature conditions. Therefore, the temperature window in my experiments was in the range 1000°C – 1150°C; that was optimal for the formation of graphene islands with disordered graphene around the islands.

3. The low pressure is confirmed to be an important factor for the formation of graphene on Re surface to avoid the dissolution of the excess of carbon into the bulk and to decrease the nucleation density of graphene sites.

4. In general, after the growth, the surface consisted of three different phases. Graphene islands, surrounding areas with defective monolayer graphene, and sites covered by amorphous carbon. Graphene islands are mostly polycrystalline – areas with bi- and multilayer graphene coexist with regions covered by a single graphene layer.

5. After the observations and comparisons of the results of graphene formation on Ta and Re foils the following can be concluded. On carbide-forming refractory metal (Ta), the carbon segregation during the cooling is less likely to occur. The monolayer of graphene can be formed only at the highest temperature. For Re, which does not form any carbides, on the other hand, the growth temperature has to be limited in order to avoid the increase in carbon dissolution away from the regime of multilayer formation.

6. The deposition of graphene multilayers, though, is more desirable in terms of protective properties for both of the studied metals.
8. THESIS SUMMARY AND OUTLOOK

In this thesis, I investigated the mechanisms of graphene formation on transition metals as well as the protective properties of graphene.

Regarding the graphene growth on Cu, the results were consistent with the reported works on this specific object. Cu foil is considered the ideal substrate to grow the monolayer graphene if all the necessary well-known growth parameters are applied. The high temperature, low pressure, individually established gases ratio (and partial pressure for each of the gases), as well as the growth time, are the necessary conditions. However, these seemingly well-studied conditions are not enough to achieve the goal – the defect-free large area of the graphene monolayer.

Even the well-studied Cu may deviate from the expected results and give poor reproducibility if the recipe is poorly adapted. There are no generally accepted standards for obtaining the required quality of graphene since the CVD systems vary among research groups. This work also discusses the questions related to the formation of multilayer graphene on Cu. The statement about the self-limiting mechanism of the formation of graphene is not final since the multilayer formation was observed on partially covered Cu foil. In addition, the deposition of graphene flakes on both sides of the Cu enclosure suggests that carbon species can diffuse through the Cu foil; thus, the segregation mechanism of graphene formation, perhaps, can be applied.

The corrosion test with Cu was not performed in this work, because (i) - the studies regarding this application of graphene are well-understood and there are less ambiguities, (ii) - it was not part of the research work but rather testing the CVD system. Briefly, graphene can protect Cu foil against some types of corrosion for a short-term period. The limited period of graphene protection is attributed to the presence of defects in the deposited graphene.

In this work, I investigated the possibility to grow graphene from a liquid source (blood) which has never been used before, to the best of my knowledge. The work was done successfully, and the fabricated device based on blood-grown graphene showed the doping by iron, which was anticipated.

In Chapter 5, the application of CVD grown graphene was demonstrated based on collaborative work with the research group from the University of Nottingham. Novel hybrid InSe/graphene phototransistor devices were demonstrated. The hybrid phototransistor devices were made by a simple microfabrication process and offer a flexible route to the integration with existing silicon manufacturing technologies. Future research can include the study of the charge transfer in other multilayer heterostructures, for instance in
InSe/hBN/graphene stack, to explore controlled charge transfer between graphene and InSe through a tunnelling hBN barrier.

In the next two Chapters, the mechanism of graphene formation on transition metals Ta and Re, as well as the testing of anticorrosion properties of graphene are presented. Ta and Re are both transition metals, but they have a different affinity to carbon and, consequently, different mechanisms of graphene formation.

The mechanism of graphene formation on Ta relies on the initial carbide formation followed by a subsequent graphene growth (predominantly monolayer). The stage of surface carbide formation is unavoidable; tantalum readily forms carbides already at 950 °C using CH₄ as a carbon precursor. The mechanism of graphene formation on Ta could be similar to that on group VIII metals (like Ni) in terms of carbon adsorption. At high temperatures, both can catalyse the graphene deposition from hydrocarbons and absorb some carbon into the bulk.

The difference between the Ta and Ni is that in the case of Ta carbon is bond chemically and carbon adsorption is irreversible with respect to temperature changes. As it is well known about Ni, upon cooling carbon segregates on the surface. Therefore the formation of carbides hinders the excess carbon precipitation during the cooldown stage, resulting in single layer graphene.

In this study, the presence of carbides on Ta was considered as a helpful step since the combination of carbide and graphene showed excellent anti-corrosion performance.

In Chapter 7, I considered the mechanism of graphene growth on Re. Rhenium, having the second highest melting point (after tungsten) has a strong affinity to carbon. The solubility of carbon in Re lies between that for Cu and Ni, but the certain value was not found due to conflicting information in different sources. Despite the high carbon solubility, Re, opposite to Ta, is not a carbide-forming metal.

I found that graphene grown on Re is mostly monolayer, although the significant areas of bilayers and multilayers were also present. The tendency of having a better quality of CVD graphene at higher temperatures, however, cannot be applied to Re. On the opposite, the higher the temperature was applied, the more multilayer patches (sometimes close to graphite) were found after the growth. This is obviously due to a large amount of carbon dissolved at high temperature, which segregates at the surface during cooling. When relatively high pressure was applied alongside with the high temperature, there was no graphene found on the Re surface, only amorphous carbon and soot.

Unfortunately, despite the multiple tries, the full coverage of graphene on Re was not achieved and only Re samples partly covered by graphene islands were undergone the corrosion tests. The results showed that even islands of graphene could perfectly protect the Re surface in a very aggressive environment – concentrated nitric acid. The protection was, indeed, a short-term but it was enough to compare results of the same corrosion tests with the bare Re foil.
To sum up, CVD is a complex process where many parameters contribute, such as growth temperature and pressure, chamber geometry, the position of the substrate during the growth, gas residence time, gas flow rate, substrate material and thickness. As a conclusion of this work, it could be stated that the key parameter of graphene formation is carbon solubility in metal. Carbon solubility in a particular metal is, obviously, the temperature dependent process, but it eventually defines the resulting mechanism of the formation of graphene.

Excellent protective properties of graphene have once again been demonstrated, at least for a short-term period, which, nevertheless, is sufficient for protection during radioisotope production and purification.
9. REFERENCES


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