

CHEMICAL VAPOUR DEPOSITION OF GRAPHENE ON COPPER-NICKEL ALLOY

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SCHOOL OF MATERIALS

I. Contents

I. Contents.....	1
II. Abstract.....	3
III. Declaration	4
IV. Copyright	5
V. Acknowledgements	6
VI. Dedication.....	7
1. Introduction and Aims.....	8
2. Literature Survey.....	10
2.1. Carbon allotropy	10
2.2. Graphene	12
2.2.1. Electronic structure of graphene	12
2.2.2. Optical properties	13
2.2.3. Mechanical properties	14
2.2.4. Thermal properties	16
2.2.5. Electrical properties	18
2.3. Graphene synthesis methods	19
2.3.1. Chemical Exfoliation.....	20
2.3.2. Mechanical cleavage	21
2.3.3. Epitaxial growth of graphene on SiC surface	23
2.3.4. Chemical Vapour Deposition (CVD).....	23
2.3.4.2. Kinetics of CVD.....	25
2.3.5. Parameter space of CVD graphene	29
2.3.6. Mechanism of CVD graphene growth	35
3. Methodology	38
3.1. Introduction	38
3.2. CVD system	38
3.3. Growth procedure	42
3.4. Film Characterisation.....	46
3.4.1. Raman Spectroscopy	47
3.4.2. Scanning electron microscopy (SEM)	49
3.4.3. Glow discharge optical emission spectroscopy (GDOES).....	51

4. CVD of graphene on pure metals	55
4.1. Introduction	55
4.2. Interaction of carbon with transition metals.....	56
4.3. CVD growth of graphene on Copper	58
4.3.1. Impact of copper substrate thickness	63
4.3.2. Possible growth mechanism	66
4.3.3. Growth at different temperature and pressure	69
4.4. CVD growth of graphene on Nickel	71
4.4.1. Impact of cooling rate	77
4.4.2. Effect of growth pressure	79
4.5. Conclusion.....	81
5. CVD of graphene on Cu-Ni alloys	83
5.1. Introduction	83
5.2. Results	85
5.2.1. Raman spectroscopy.....	85
5.2.2. Effect of cooling rate.....	90
5.2.3. GDOES results.....	93
5.3. Conclusion.....	102
6. CVD process simulation.....	103
6.1. Introduction	103
6.2. Thermodynamics	104
6.3. Fluid flow and heat transfer	110
6.3.1.Setting COMSOL Multiphysics	110
6.3.2.Results.....	115
6.4. Gas-Phase Reaction kinetics	119
6.4.1.Results.....	122
6.5. Chemical surface reactions	127
6.5.1.Results.....	131
6.6. Conclusion.....	133
7. Conclusion.....	135
8. Further Work.....	139
9. References	141

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II. Abstract

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Among all the methods of produce graphene, chemical vapour deposition (CVD) is the most promising route, due to the high quality of the graphene film produced and the large scalability. The mechanism of graphene growth by CVD on a metal substrate is believed to be controlled by its solubility for carbon with precipitation dominant at high carbon solubility and surface diffusion at low solubility. This thesis is exploring the impact of C solubility in the catalytic substrates, on the CVD growth of graphene. Cu-Ni alloys show complete solid solubility across their composition range and can be used to explore the influence of C solubility on graphene growth. Graphene is grown on Cu-Ni alloys of composition Cu, Cu₇₀-Ni₃₀, Cu₅₅-Ni₄₅, Cu₃₃-Ni₆₇ and Ni in a hot-wall CVD reactor.

Firstly, the growth was achieved on pure metals (Cu and Ni) using CH₄ as a C source and the produced film was characterised by Raman spectroscopy and scanning electron microscopy (SEM). The C profile within the substrate bulk was measured by glow discharge optical emission stereoscopy (GDOES). The latter showed the difference in bulk C content between Cu and Ni, which reflects the influence on the graphitic film on the surface.

The CVD growth of graphene on Cu-Ni alloy showed a transition from bilayer graphene (BLG) to few layer graphene (FLG) surface coverage when the Ni content increased, which is accompanied by an increase in the diffusion of C in the bulk and incubation time. The cooling rate showed a significant effect on the graphene surface coverage; however, the influence varied with Ni content.

The fluid flow simulation indicated that the gas velocity beneath the substrate is very low which results in a lower mass transfer to the bottom substrate surface. Gas-phase kinetics simulation reveals the impact of gas residence time on the concentration of active species; moreover, the concentration increases down the stream of the flowing gas. Finally, the surface reactions of the CH₄/H₂ mixture model showed a good agreement with the experimental observations under low growth pressure; however, it failed at high growth pressure.

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VI. Dedication

To my Family

1. Introduction and Aims

Chemical vapour deposition (CVD) is considered the most promising method of large-scale production of graphene film ¹. Since the first successful attempt of CVD growth of graphene by Somani in 2006 ², there was an extensive research effort to produce large areas of graphene for industrial applications. Even though a 30-inch single layer graphene (SGL) was produced by CVD method ³, the mechanism of graphene formation is still not fully revealed. The graphene growth by CVD route was proposed to be either surface adsorption or C segregation process based on the C solubility of the substrate material. However, a study focusing on the role that C solubility plays in the growth of graphene film by CVD is needed.

This thesis has two aims. The first is the understanding of the role that C solubility has on graphene growth by CVD. The methodology adopted in this work is to grow a graphitic film on catalytic substrates using Cu-Ni alloys, as a model catalyst system, which have C solubility values between Cu and Ni C solubility values.

The second aim is to simulate the CVD process including fluid flow, heat transfer, gas-phase chemistry, and surface reactions. Rather than calculating the fluid flow parameters, in this thesis fluid flow package (COMSOL) was used to visualise the fluid behaviour at any point in the reactor, in particular on the substrate position, to give a better understanding of the contribution of the fluid flow in the deposition process. Further, this thesis investigates the gas phase kinetics in the CVD reactor, which highlights the impact of reactor geometry. Developing an understanding of the role of C solubility in CVD graphene will not only assist in a better knowledge of the growth mechanism of graphene, but it control the number of graphene layers which is an important aspect in electronic applications. Furthermore, modelling fluid dynamics, heat

transfer, gas-phase chemistry and surface chemistry and their impact on the growth mechanism will help in controlling growth process and assist in on other CVD reactions design.

2. Literature Survey

2.1. Carbon allotropy

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 configurations⁴. The electronic configuration of carbon atoms is $[\text{He}] 2s^2 2p^2$ with four valence electrons in the ground state. Carbon tends to hybridise in one of three known forms: sp , sp^2 and sp^3 (Figure 2.1). The sp^3 bond structure forms when four valence electrons are oriented in orbitals parallel to the vertices of a tetrahedron. This allows the formation of four strong σ -bonds with the neighbouring atoms at an angle of separation of 109.5° . Diamond is an example of a material formed from sp^3 carbon hybridization. In the sp^2 configuration, however, three of the valence electrons are arranged in a plane parallel to the vertices of a triangle. This enables each carbon atom to covalently bond with three adjacent atoms in the hexagonal network through three σ -bonds in a plane with an angle of 120° between them, while the fourth valence electron is assigned to the π orbital that lies perpendicular to the σ -bonding plane. The π -bond is significantly weaker than the σ -bond. Graphite is an example of a material formed from sp^2 carbon, with three strong σ -bonds in the X-Y plane and one weak π -bond normal to the plane which holds the adjacent graphite layers together. In the third configuration, sp , where two valence electrons form a σ -bond along the $\pm x$ -axis, with the remaining two electrons lying in the y and z-direction forming the $p\pi$ bond, an example of sp hybridization is found with the alkynes (C_2H_2). The variety in carbon hybridisation is reflected on the physical properties of carbon forms, *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 (π bonding) is grey, soft and electrically conductive.

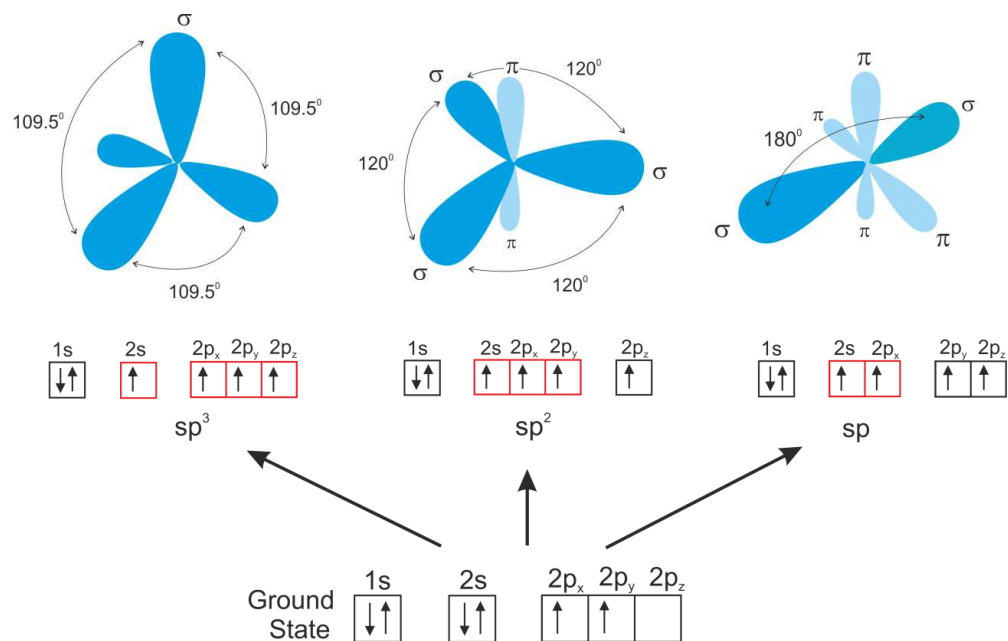


Figure 2. 1. Illustration of carbon atom ground and hybridise state with the bonding orbitals for sp , sp^2 and sp^3 hybridization. Adopted from ⁵.

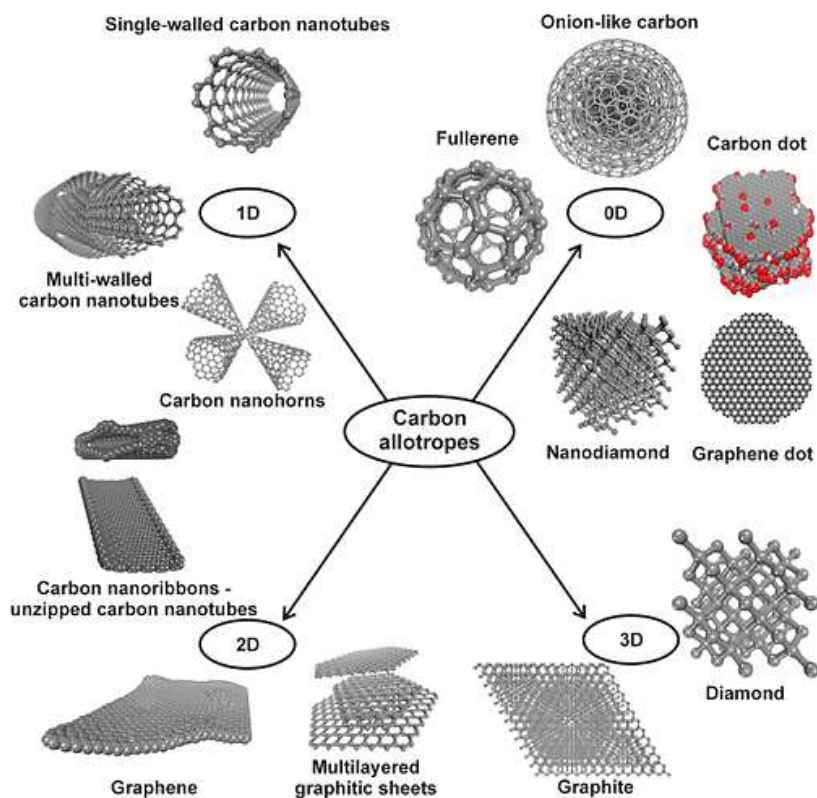


Figure 2. 2. Carbon allotropes classification based on their hybridization and type of bonding ⁶.

Carbon allotropes classified according to their dimension; (zero-dimension) 0D, (one-dimension) 1D, (two-dimension) 2D and (three-dimension) 3D (Figure 2.2). Fullerenes, nanotubes, graphene, and diamond are examples of the stated dimension classification respectively ⁶.

2.2. Graphene

2.2.1. Electronic structure of graphene

Graphene is a single graphite layer where the atoms are arranged in a hexagonal (honeycomb) crystal lattice. The strong covalent bond between carbon atoms in graphene results from atoms sharing one s and two p orbitals of the neighbouring atoms, to form a sp^2 bond with a bond length of 1.42 Å. The graphene cell comprises two interpenetrating triangular Bravais lattices, A and B, with one carbon atom per sublattice (Figure 2.3(a)). The reciprocal lattice of graphene crystal is also hexagonal with a high symmetry. The centre point of the reciprocal lattice is defined as Γ and the corner points are denoted K and K'. A simple tight-binding Hamiltonian can describe the electronic structure of graphene crystal (Figure 2.3(b)), where the electronic wave functions from different atoms overlap. σ -bands are neglected in the calculation because σ - and σ^* - energies are far from the Fermi level. By symmetry, the overlap between $p_z(\pi)$ and s , p_x and p_y bands is zero. In contrast, overlapping unhybridised $2p_z$ electron orbitals of nearest carbon atoms form π - and π^* - bands, which intersect at the corners of the Brillouin zone (K and K' points) to create a conical energy spectrum called the Dirac cone ⁷. The bottom half of the energy cone is fully occupied with electrons (valence band), while the top is empty (conduction band). Graphene is considered a zero-bandgap semiconductor or a semimetal material where the Fermi level (E_F the zero energy reference in Dirac cone defined by K and K') is reduced to the six corners of the Brillouin zone. Graphene quasi-particles show a linear dispersion relation (the relation

between energy, E , and momentum, $\hbar k$, at K and K') as if they are massless relativistic particles:

$$E(k) = \pm \hbar v_F k \quad 2.1$$

where v_F is the Fermi velocity ($\sim 10^6$ m/s) and k is the momentum. It is well known that electrons in all condensed materials follow Schrödinger's equation and that any relativistic effects are unimportant. However, the case of graphene is different because it follows Dirac's equation (they act like a zero-mass particle at constant velocity). Therefore, graphene has a variety of interesting electronic properties, including a high charge mobility μ ($200000 \text{ cm}^2/\text{Vs}$)⁸ and an ambipolar electric field effect^{9,10}.

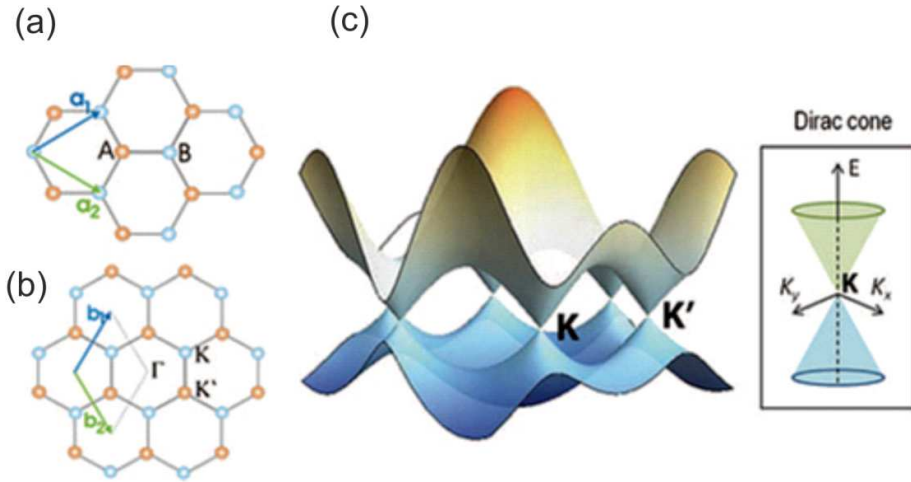


Figure 2. 3. (a) Graphene crystal structure composed of two sub-lattices A and B. (b) Brillouin zone of graphene. (c) Band structure of graphene calculated by tight-binding Hamiltonian shows a linear electronic structure that represents Dirac cone at Brillouin zone corners (insert). Figure from⁹

2.2.2. Optical properties

Monolayer graphene absorbs 2.3% of incident light over a wide wavelength range¹¹ thus making it difficult to detect by optical microscopy on transparent substrates (e.g. glass) or opaque substrates (e.g. metal). Many reports confirm graphene on Si/SiO₂ can be imaged by optical microscopy due to interference phenomena^{3,12}. Monolayer graphene

has a constant absorption coefficient at wavelengths from 300 to 1000 nm, and it is maximum at 250 nm due to the transition of the unoccupied π^* states¹³ (Figure 2.4). Graphene's unique optical properties are a result of the linear electronic structure, and these fascinating properties have various applications, especially if the optical and electronic properties are combined together.

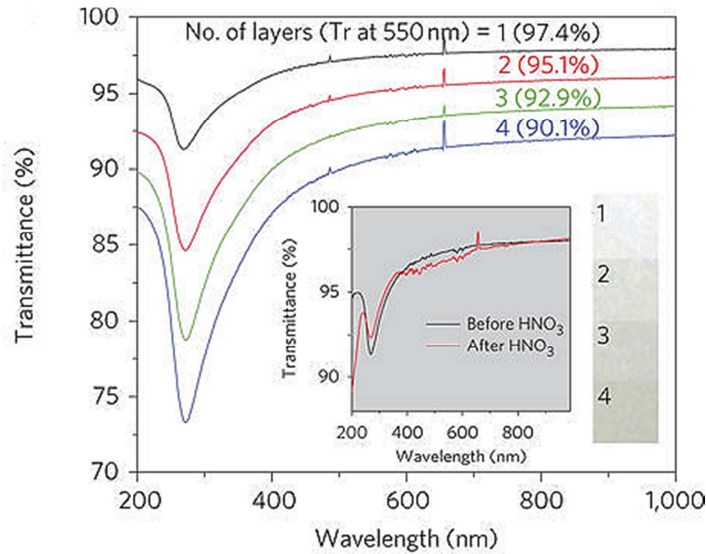


Figure 2. 4. UV-vis spectra of CVD graphene transferred by roll-to-roll layer-by-layer technique on a quartz substrate. The inset shows the UV spectra of graphene films doped with HNO₃. The right inset shows optical images of the transferred layers (1×1 cm²). Figure from³.

2.2.3. Mechanical properties

The first experimental measurement of the mechanical properties of single-layer graphene was reported by Lee et al.¹⁴ in 2008, who used an atomic force microscopy (AFM) to indent graphene placed over an array of circular wells (Figure 2.5). The graphene showed a nonlinear elastic stress-strain response with Young's modulus of $E = 1.0$ TPa, a third-order elastic stiffness of $D = -2.0$ TPa, and an intrinsic strength of $\sigma_{\text{int}} = 130$ GPa. These superior mechanical properties are promising for application in composite. The mechanical properties of composite materials are found to depend on the concentration of the reinforcement phase (graphene)¹⁵, the dispersion state of graphene¹⁶ and the length to the thickness ratio (aspect ratio) of the reinforcement

materials^{17,18}. The increase in the graphene concentration increases tensile strength of the graphene-polystyrene (PS) composite as shown in Figure 2.6(a)¹⁹.

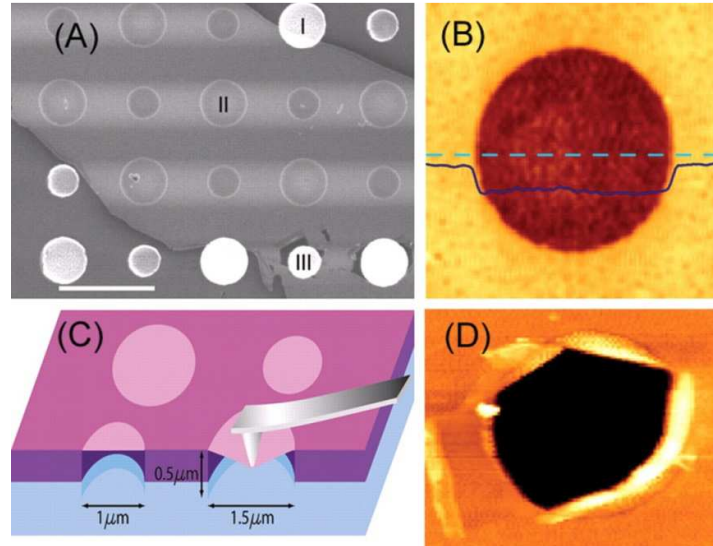


Figure 2. 5. Measurement of suspended single layer graphene mechanical properties. (a) Scanning electron microscopy (SEM) image of graphene flake covering an area of an array of circular wells. (b) AFM image of nanocontact mode of one membrane, the blue line is a height profile. (c) Schematic of AFM nanoindentation technique. (d) AFM of a fractured graphene. Figure from reference¹⁴.

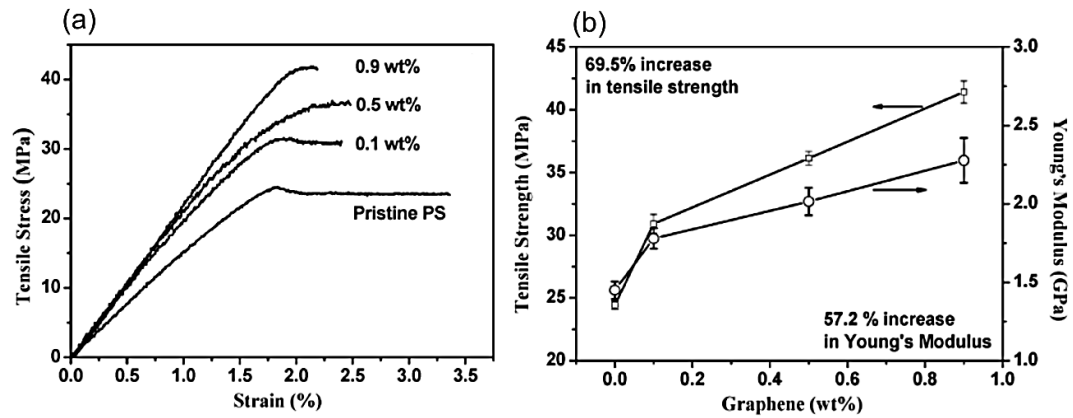


Figure 2. 6. (a) Stress-strain curve of graphene-polystyrene (PS) nanocomposite with different graphene sheet contents. (b) Effect of graphene sheet content on Young modulus and tensile strength. Figure from²⁰.

The graphene oxide (GO)/polymer composites show an enhancement in mechanical properties. For instance in a GO/PVA composite the elastic modulus and strength was found to increase by 76 % and 62 % respectively by adding 0.7 wt.% of GO²⁰. This

high specific increase is due to the functional groups on graphene surface leading to a high level of dispersion of graphene in polar solvents and enhanced polymer-graphene interaction.²⁰

2.2.4. Thermal properties

Carbon allotropes have a broad range of thermal conductivity (K), from 0.01 W mK^{-1} (for amorphous carbon) to more than 2000 W mK^{-1} (for diamond and graphene), Figure 2.7²¹. The heat transfer in solid materials is governed by acoustic phonons and electrons; therefore the thermal conductivity is contributed by both electrons (K_e) and phonons (K_p). The electronic contribution (K_e) to the thermal conductivity in metals is very high because of a large number of free carriers. For example, the thermal conductivity of copper at room temperature is $\sim 400 \text{ W mK}^{-1}$, and the K_e contribution is almost 98 % of this total. In carbon materials, thermal conductivity is usually due to the lattice vibrations and therefore the phonon contribution, despite graphite's metal-like properties. This results from the strong covalent sp^2 bonding and K_e can be significant if the materials are doped with impurities²¹. The first experimental study to measure the thermal conductivity of single-layer graphene was reported by Balandin and co-workers²². Figure 2.8 illustrates the method used; a suspended single-layer graphene flake was heated by a 488 nm laser and the change in the local temperature was monitored by measuring the shift in the G peak position. The thermal conductivity value measured by this method was $\sim 4840 - 5300 \text{ W mK}^{-1}$, which is higher than the values recorded for single-wall carbon nanotube (SW-CNT), $\sim 3500 \text{ W mK}^{-1}$ ²³, and multi-wall carbon nanotube (MW-CNT), 3000 W mK^{-1} ²⁴. This interesting property attracted researchers to couple graphene with polymer matrices, such as epoxy resin²⁵, polypropylene (PP)²⁶, polyvinyl chloride (PVC)²⁷ and polycarbonate (PC)²⁸ to enhance heat transfer for electronic circuit applications. However, enhancement in thermal conductivity is not as dramatic as electrical conductivity, because the difference in thermal conductivity

between graphene and the polymer is 4 in the order of magnitude ($K_{\text{graphene}}/K_{\text{polymer}}$), while for electrical conductivity ($\rho_{\text{graphene}}/\rho_{\text{polymer}}$) it is approximately 15-19 in the order of magnitude²⁹.

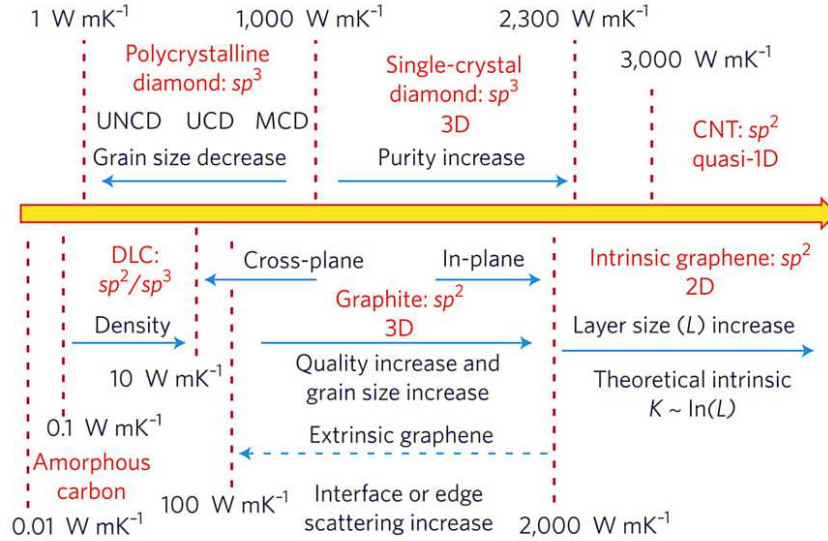


Figure 2. 7. Diagram of the reported thermal properties values of carbon allotropes. The axis is not to scale. From reference²¹.

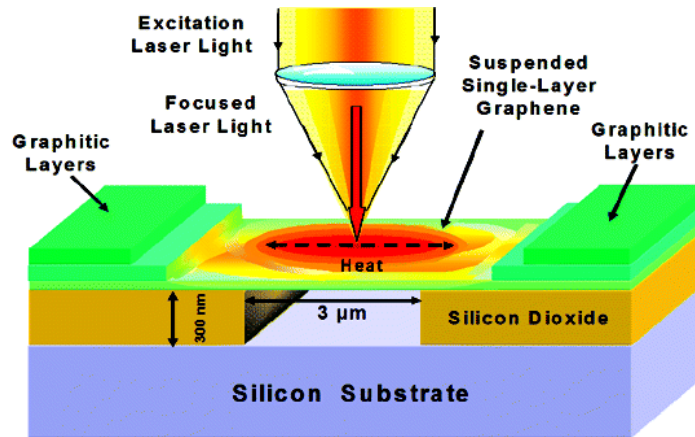


Figure 2. 8. Schematic of optothermal Raman method to measure graphene thermal conductivity. The 488 nm focused laser light generates a heat wave inside single-layer graphene which then propagates toward the heat sinks. Figure from reference²².

2.2.5. Electrical properties

The intrinsic electronic behaviour of graphene is a semi-metal or zero bandgap semiconductor behaviour, due to the contact of the conduction and valence bands at the six Dirac points³⁰. Furthermore, the linear dispersion relationship between momentum and energy enables the charge carriers to travel with zero effective mass (m^*) with a Fermi velocity $\sim 10^6 \text{ ms}^{-1}$. The band structure of graphene is responsible for its unique electronic properties including its high charge mobility at room temperature ($\sim 15000 \text{ cm}^2 (\text{Vs})^{-1}$)³¹ and room temperature Hall effects³². However, the zero bandgap electronic structure of graphene is not suitable for nano-electronic applications. It is theorised that a band gap in graphene can be opened via three possible routes: geometry restriction by reducing the size of a large graphene sheet into one dimension direction; using AB stack Bilayer graphene (BLG); lastly by subjecting graphene to strain. Theoretical predictions claim that graphene's band gap can be modified by reducing large-area graphene in one dimension, *i.e.* forming graphene nanoribbons^{33,34}. It is found that the band gap is inversely proportional to the width of nanoribbons for types, zigzag and armchair. It is experimentally proved that a bandgap of 200 meV can achieve for nanoribbon width below 20 nm³⁴.

Table 2. 1. Graphene bandgap opening ways. Table from³⁵.

Graphene type	Size	Bandgap	Remarks	Ref.
SLG†† on SiO ₂	LA*	No	Experiment and theory	31,36
SLG on SiO ₂	GNR†	Yes	Experiment and theory, gap due to lateral confinement	33,34
BLG on SiO ₂	LA	Yes	Experiment and theory; gap due to symmetry breaking by perpendicular interlayer field	37–39
Epitaxial SLG	LA	Yes	Experiment and theory, gap due to symmetry breaking	40
		No	Experiment and theory	41
Epitaxial BLG	LA	Yes	Experiment and theory	42,43
Epitaxial SLG, BLG	GNR	Yes	Theory	43
Strained SLG	LA	Yes	Theory; gap due to level crossing	44

*LA: large area, †GNR: graphene nanoribbon, ††SLG: single layer graphene

BLG³⁹, is a promising way to achieve a bandgap despite it is initially being a gapless band structure, however, when an electric field is applied normal to the BLG, a band gap opens up to 200-250 meV for high-applied fields³⁷. Finally, the influence of strain on a graphene sheet has been simulated as a mean to tune the band gap. However, a uniaxial strain of $\sim 20\%$ is required, which is difficult to achieve experimentally^{45,46}. Table 2.1 is a review of reported possible ways to open graphene bandgap.

2.3. Graphene synthesis methods

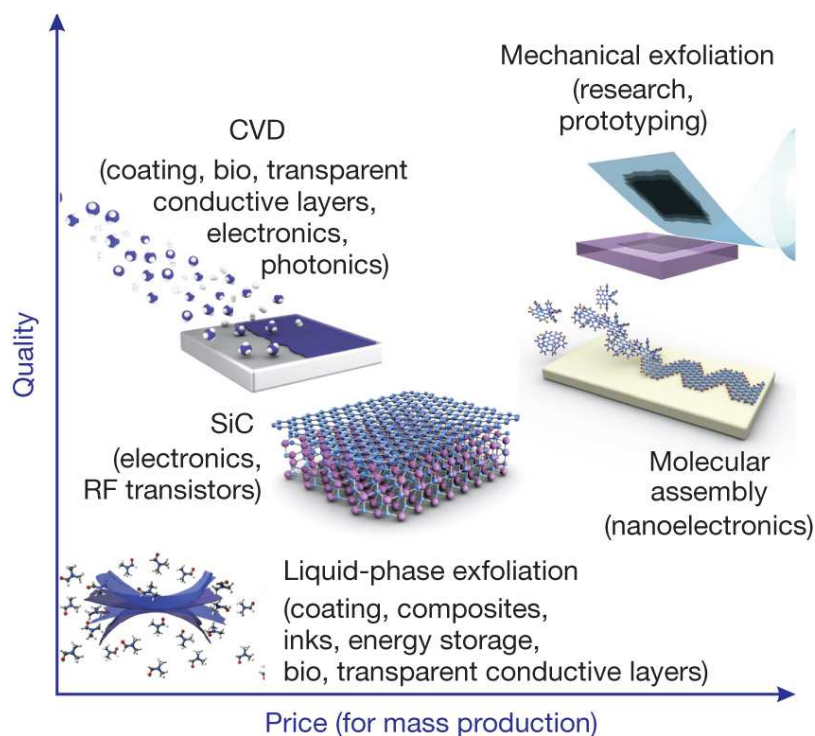


Figure 2. 9. Schematic plot shows graphene different synthesis methods with their correspondence mass-production price and quality. Figure from ⁴⁷.

Since the first successful report of the isolation of graphene from graphite in 2004³¹, several methods have been proposed for graphene synthesis. All the established methods lie in one of the two categories; top-down or bottom-up. For the top-down approach, graphene fabrication starts with three-dimension bulk graphite with the aim of

isolating individual two-dimension graphene sheets (e.g. chemical exfoliation and mechanical cleavage). In contrast, the bottom-up approach involves growing the graphene sheet from its constituent building blocks (atoms or molecules) on a supportive substrate, such as in the chemical vapour deposition method. Figure 2.9 shows the main techniques used to produce graphene which will be presented briefly in the following paragraphs.

2.3.1. Chemical Exfoliation

Synthesis of graphene by chemical exfoliation of graphite has three main routes: direct sonication of graphite in an organic solvent or surfactant solution ^{48,49}, electrochemical exfoliation of graphite ⁵⁰ and intercalation-exfoliation of graphite ⁵¹ (Figure 2.10). Chemical exfoliation includes two steps: the first step is to increase the spacing between graphite layers, therefore reducing the van der Waals forces between each layer to produce a “graphene-intercalated compound (GIC)”. The second step is to exfoliate the GIC to graphene and this typically achieved by either rapid heating or sonication ⁵². Single layer graphene oxide is considered an example of the chemical exfoliation route ⁵³.

Boehm et al. found in 1962 that few carbon layers can be produced by reducing a dispersion of GO either by chemical or by thermal methods ⁵⁴. The process of graphite oxidation goes back to 1859 when Brodie first oxidized graphite using potassium chloride and nitric acid ⁵⁵. Staudenmaier, forty years later, enhanced Brodie’s technique by adding sulphuric acid to get a low pH and feeding potassium chloride in multiple parts over the reaction course ⁵⁶. The Hummers method is the most common one used to oxidize the graphite ⁵⁷. Based on the Hummers method, graphite oxide can be synthesised by using concentrated sulphuric acid, potassium permanganate and nitric acid as oxidants ²⁹. Ruoff et al. prepared monolayer graphene by the reduction of

graphite oxide in 2006. Ruoff's method consists of strongly oxidizing graphite powder, followed by ultrasonication in aqueous solution to separate the GO layers to monolayers and finally treating the resulting GO monolayer with hydrazine (N_2H_4) to form graphene⁵⁸.

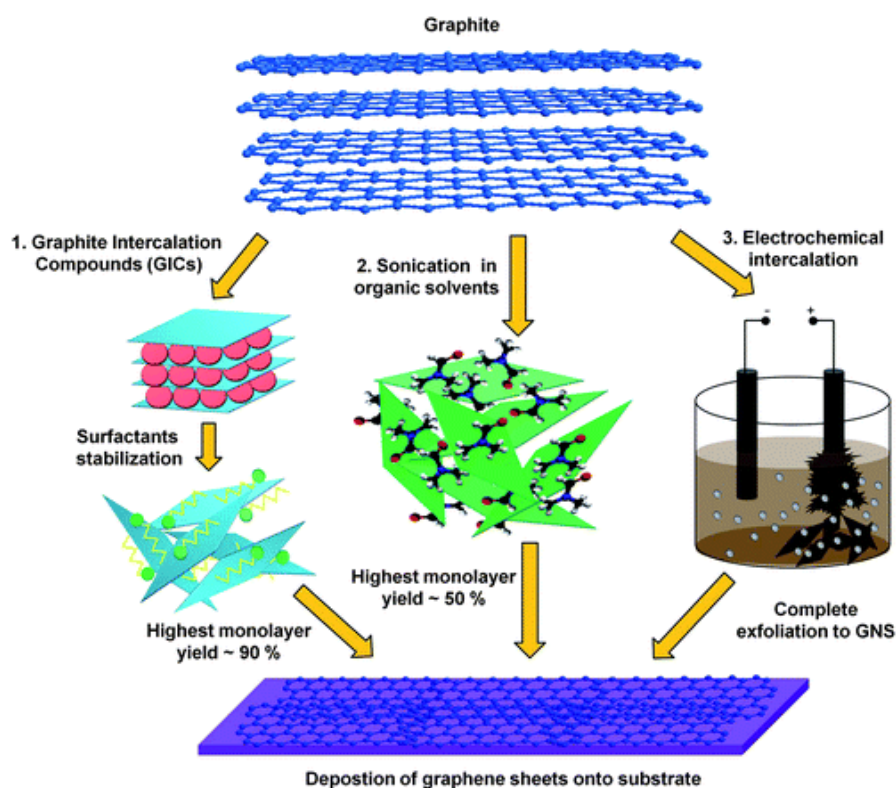


Figure 2. 10. Schematic shows the three routes of graphene exfoliation. Figure from reference⁵⁹.

2.3.2. Mechanical cleavage

The mechanical cleavage method (or as the media calls it the “Scotch Tape method”) is considered to be the first successful method used to isolate graphene layers from graphite⁵⁷.

Novoselov et al. used 1mm thick platelets of highly-oriented pyrolytic graphite (HOPG) that were etched in an oxygen plasma to prepare mesas (5 μm deep and a various square size from 20 μm to 2 mm)³¹. A 1 μm thick photoresist wet film spun over a glass

substrate is used to attach the mesas by pressing the structure against the film. After attaching the mesas to the photosensitive film, it is easily peeled off from the HOPG structure. Scotch tape is then used to repeatedly peel off flakes of graphite from the mesas. The final retained thin flakes were released in acetone and were later captured by dipping a silicon wafer in the solution, followed by washing in water and propanol.

Geim and his group reported another method which is as similar as drawing with chalk on the blackboard⁶⁰. Two fresh surfaces of layered crystals, e.g. graphite, were rubbed against each other and the result is a variety of flakes attached to the surface. These layers were found to consist of few-layers and monolayers of graphene. Following this work, several attempts were made to enhance the efficiency of the mechanical exfoliation, such as involving ultra-sonication⁶¹, an ultra-sharp diamond wedge⁶², electrostatic force⁶³ and a transfer printing technique⁶⁴. Mechanical exfoliation is a low budget technique, and the quality of produced graphene is high; however, controlling the produced graphene layer is challenging, plus the flakes are randomly distributed on the substrate. Therefore, this method is suitable for research but not for commercial production.

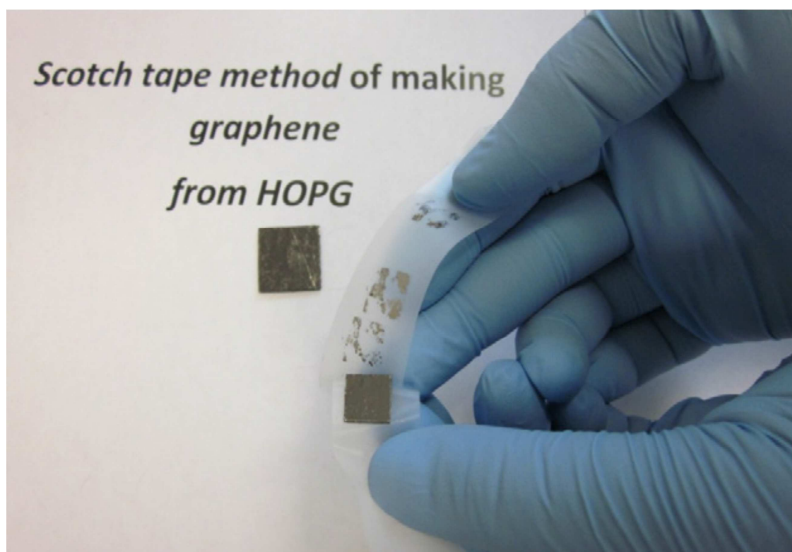


Figure 2. 11. Mechanical exfoliation of graphene by repeated peeling of HOPG using scotch tape. Figure from²⁹.

2.3.3. Epitaxial growth of graphene on SiC surface

The epitaxial thermal growth of a graphite layer on a single crystal silicon carbide was first reported by Bommel et al. in 1975⁶⁵. Epitaxial growth of 1-3 graphene sheets thin film, was first reported by De Heer et al. in 2004 on a single crystal 6H-SiC (0001) surface⁶⁶. Epitaxial refers to a process of depositing a single crystalline film onto the surface of a single crystal substrate. Moreover, 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 layer⁶⁶. This process is very attractive for the semiconductor industry because it produces graphene on silicon and thus there is no need to transfer the graphene to another substrate after growth. The process takes place under ultra-high vacuum conditions (UHV) and high temperature (1200 °C); when SiC anneals under these conditions silicon atoms evaporate and leave carbon atoms which in turn arrange to form a graphene layer^{29,67}. Therefore the nature of the graphene film depends on the annealing temperature and time. This method is very promising for the electronic industry, but it has many drawbacks. For example, the graphene produced is rotationally disordered, and the vertical roughness of the graphitic film is not uniform⁶⁸. Due to the high temperature high vacuum conditions, the production of large area graphene and controlling its physical and electronic properties are challenging²⁹.

2.3.4. Chemical Vapour Deposition (CVD)

Chemical vapour deposition (CVD) is used to manufacture powders, coatings, fibres and monolithic components. Most metals and non-metallic elements such as carbon and silicon can be made by CVD, as well as a large number of compounds including carbides, oxides and nitrides. CVD is defined as the deposition of a solid resulting from chemical reactions in gasses on hot surfaces⁶⁹.

The CVD dates to the latter part of the nineteenth century, when Sawyer and Man filed a patent in 1880 for their work to improve the quality of an illuminating conductor for electric lamps by covering it with carbon from hydrocarbon decomposition at high temperature ⁷⁰. In 1896 Aylsworth successfully deposited refractory metal by heating a substrate in a vapour containing the desired element ⁷¹. It was not until the 1930s when further progress was made, when deposition of some materials and compounds was commercially demanded ⁷².

CVD of graphitic films on metal substrates was first reported by Lang in 1975 ⁷³. He found that by flowing ethylene (C_2H_4) over a hot platinum surface, a graphitic layer formed. In 1979, Blakely et al. reported the formation of a graphite layer on Ni by doping Ni (111) single crystal at high temperature 927-1027 °C followed by fast cooling ^{74,75}. They found that the carbon coverage is dependent on temperature, with optimum deposition when temperature is as close as possible to equilibrium conditions.

Since the successful experiment to isolate a single graphene layer, a number of synthesis methods were proposed. However, CVD is considered the most promising method for synthesizing large areas of monolayer and few-layer graphene.

The first successful attempt to grow graphene using CVD was reported by Somani and his group in 2006 by using camphor ($C_{10}H_{16}O$) as a carbon source, and Ni foil as the hot substrate; and this resulted in the deposition of a few-layer graphene (FLG) with an interlayer spacing of 0.34 nm ². Even though the graphitic film was very thick, it showed the promise of the synthesis of monolayer graphene by CVD.

The breakthrough was by Ruoff et al. who reported the CVD of single layer graphene on Cu substrate ¹. A 25 μ m thick Cu foil was annealed in a hydrogen (H_2) atmosphere at 1000 °C, followed by introducing methane (CH_4) at low pressure. The resulting deposited graphitic film was ~ 95 % SLG with a small percentage of FLG. The

graphene film was found to be continuous over grain boundaries and Cu surface steps. Therefore, the CVD route can potentially meet the thin film applications demands for graphene, in terms of cost, quality and scalability. For example, CVD graphene film as large as 30-inch of 95% SLG coverage has been reported by Byung et al.³.

Given the focus on this thesis on CVD growth of graphene, the background literature will be reviewed in detail. The following sections will examine the key factors which influence the growth: thermodynamics, kinetics, temperatures, pressure, carbon precursor, role of hydrogen and substrate.

2.3.4.1. The thermodynamics of CVD

The thermodynamic aspect of CVD is essential to understand the chemical reaction products (it should be noted though that thermodynamics calculates the final equilibrium state of the system and not the steps and rates taken to achieve it). The uniformity and the quality of the resulting film are determined by the feasibility of the possible chemical reactions in the CVD process. It is important to know which reactions might take place so that a suitable precursor can be selected. Minimization Gibbs free energy of the gas-solid system is the basic thermodynamic calculation to determine the appropriate CVD phase diagram^{76,77}. This is useful to predict the equilibrium phases existing under the processing conditions of pressure, temperature and reactant concentrations. The first step of every designed CVD process is to evaluate the feasibility of its chemical reactions. By calculating the Gibbs free energy (ΔG_r) of the reaction, the feasibility can be concluded. If the ΔG_r is negative, then the reaction could occur while the positive value means the reaction cannot take place. Moreover, in some CVD processes several possible reactions can take place (all reactions are

thermodynamically feasible); in which case the reaction which has the lowest negative value should be considered, since it will be more stable ⁷⁸.

2.3.4.2. Kinetics of CVD

The Kinetics and mechanisms of CVD have been studied by many researchers, and their results give a better understanding of the deposition processes. The complexity of the CVD processes is a real problem for its kinetic study. Other factors also make kinetic calculations difficult, including the type of gas flow inside the reaction chamber, local temperature variation, concentration of reactant gases over the substrate and geometric effects of the chamber. Mass transport and surface kinetics are considered to be the rate-limiting factors. If the mass transport process is slow, *i.e.* if the reactant species diffuse slowly from the bulk gas flow to the substrate then it will be the rate-limiting process and vice versa ^{77–80}. Figure 2.12 summarizes the growth kinetics inside the CVD chamber.

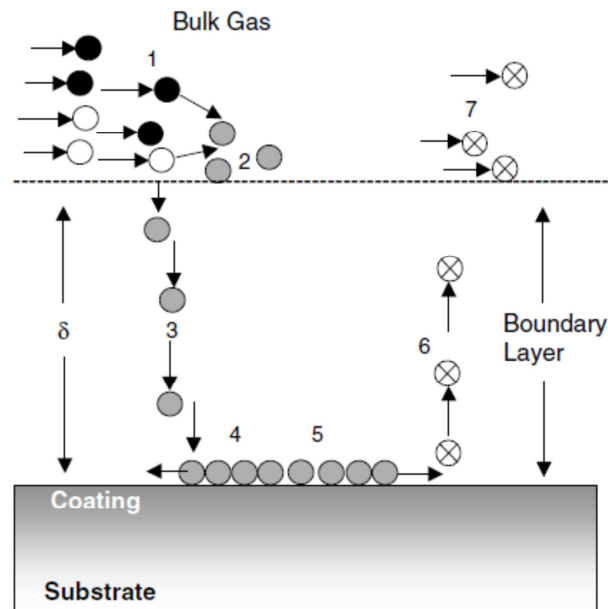


Figure 2. 12. Kinetics of CVD,(1) Delivery of reactant to the CVD chamber; (2) Intermediate reactions in the bulk gas stream; (3) Diffusion through the boundary layer,(4) Absorption of reactants on the substrate surface; (5) Reactions at the substrate surface; (6) Diffuse out of the by-products through the boundary layer; (7) Removal of the by-products. (Reproduced from ⁸⁰)

The diffusion of the reactant species from the main flow through the boundary layer is the rate-limiting step for the mass transport process. The reactant flux according to Fick's 1st law can be expressed as:

$$J_A = -\frac{D_{AB}}{RT} \left(\frac{C_{AB} - C_{AS}}{\delta} \right) \quad 2.2$$

where J_A is the flux of species A, D_{AB} is the diffusivity, C_{AB} is the bulk concentration, C_{AS} is the concentration at the surface, R is the gas constant, T is the absolute temperature, and δ is the boundary layer thickness. The boundary layer appears when the gas flow is laminar (which is the ideal case in all CVD reactions). The reactant concentration and the gas velocity are zero at the substrate surface, and they increase at the mainstream; the distance between high and zero concentration is the boundary layer thickness δ which can be calculated:

$$\frac{\delta}{x} = \frac{5.00}{\sqrt{Re}} \quad 2.3$$

where Re is Reynolds number ($Re < 2300$ for laminar flow) and x is the local distance⁸¹.

The average boundary layer can be calculated by applying the above equation for the substrate length:

$$\bar{\delta} = \frac{10}{3} \sqrt{\frac{\mu_{\text{mix}} L}{\rho U}} \quad 2.4$$

where L , is the length of the substrate, μ_{mix} is the gas mixture viscosity, U is the mainstream velocity, and ρ is the density of the gas.

According to Chapman-Enskog theory⁸², the binary diffusivity D_{AB} of reactants can be calculated using the following equation:

$$D_{AB} = 0.0018583 \frac{\sqrt{T^3 \left(\frac{1}{M_A} + \frac{1}{M_B} \right)}}{p \sigma_{AB}^2 \Omega_{D,AB}} \quad 2.5$$

where T is the absolute temperature, M is the molecular weight, p is the pressure, σ_{AB} is the collision diameter and $\Omega_{D,AB}$ is the collision integral.

The CVD kinetics (mass transport and surface kinetics) are illustrated schematically in Figure 2.13. C_g and C_s are the concentrations of gas in bulk and at the substrate surface respectively. It is clear from Figure 2.13 that the concentration of gas drops from the bulk to the substrate surface, therefore the flux of the gas is approximate:

$$J_{gs} = h_g(C_g - C_s) \quad 2.6$$

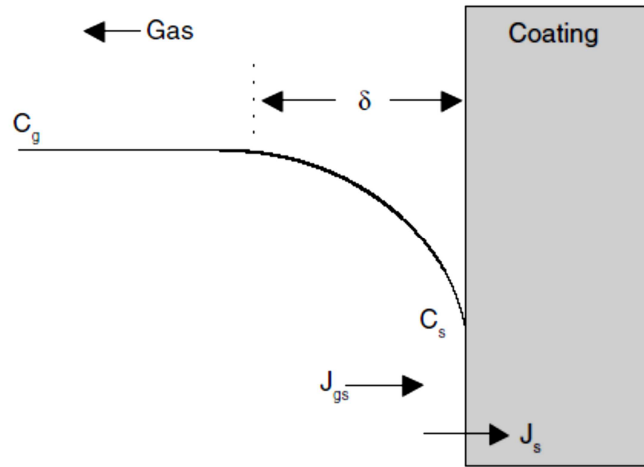


Figure 2. 13. Schematic diagram of the growth process model ⁸⁰.

where h_g is the mass transfer coefficient. The approximate flux gas consumed at the surface is related to the rate constant for the slowest surface reaction:

$$J_s = K_s C_s \quad 2.7$$

where K_s is the rate constant of the slowest surface reaction.

So according to equation 2.6 and 2.7 the two kinetic processes can be summarized as: if $K_s \gg h_g$ then the system is under mass transfer control because the mass transfer is very low from the bulk to the surface through the boundary layer. In contrast, if $h_g \gg K_s$

(this normally happen when $C_g \approx C_s$) then the process is under surface reaction control.

Figure 2.14 shows schematically how the reaction kinetics contribute to the deposition rate ⁷⁶. Moreover, the rate of the surface reaction increases with increasing temperature and the mass transfer of gas phase increases with increasing pressure ⁸⁰.

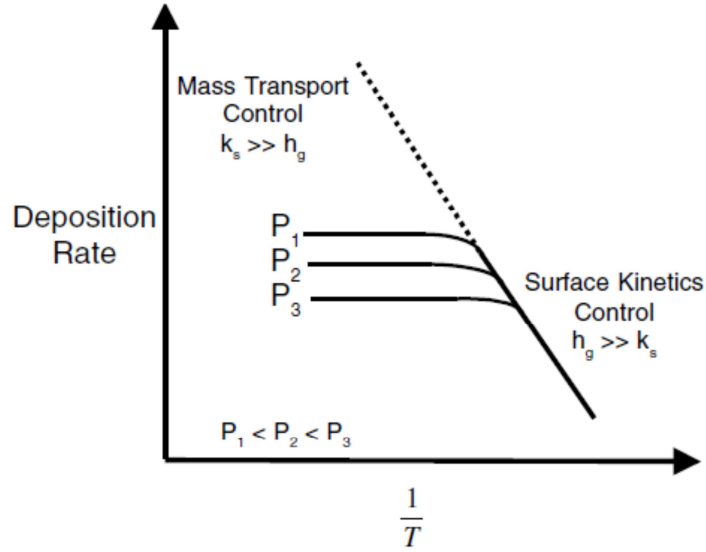


Figure 2. 14. Schematic diagram illustrating the effect of temperature, pressure and kinetics on the growth rate. ⁸⁰

2.3.5. Parameter space of CVD graphene

2.3.5.1. Temperature

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. For graphene to grow on Cu and Ni, the deposition temperature range is typically between 800-1000 °C. Hokwon et al. reported that a low growth temperature led to high nucleation density of graphene and poor graphene coverage on the Cu surface ⁸³. Furthermore, increasing the deposition temperature and time (up to 1000 °C and 30 min respectively) decreased the nucleation density and

formed continuous graphene films as shown in Figure 2.15. However, increasing temperature can also lead to poor quality graphene films, as Lili Fan et al. found that growth at temperatures near the melting point of substrate resulted in holes in the graphene film. These holes are believed to be due to the evaporation of the copper damaging the depositing film ⁸⁴. For Ni, the use of a low deposition temperature <460 °C leads to nickel carbide (Ni₃C) formation, which slowly diffuses into the bulk metal at high temperatures ⁸⁵. Most studies suggest that using 1000 °C for graphene growth on Ni is suitable, since at that temperature the solubility of carbon increases. A subsequent fast cooling rate is then crucial, to precipitate the carbon atoms out of the bulk to form graphene ^{86–91}.

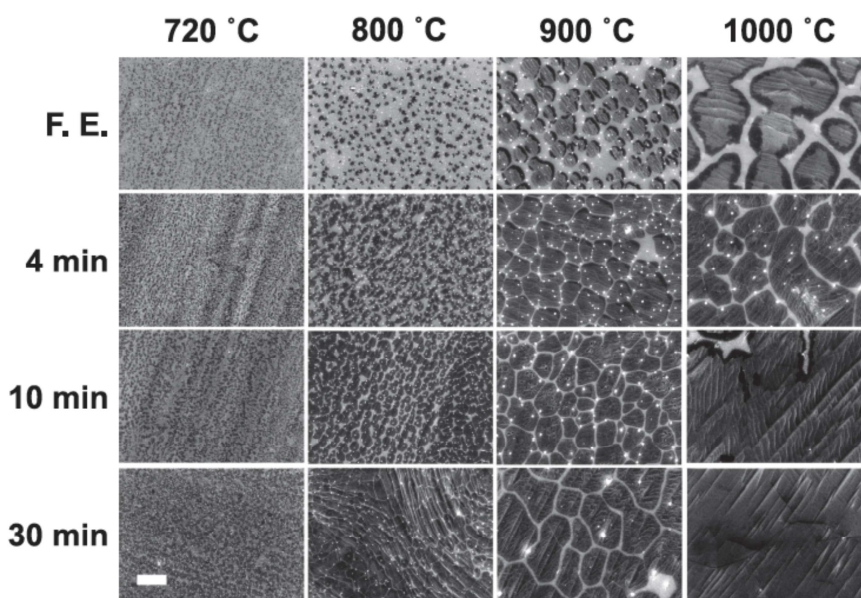


Figure 2. 15. High-resolution scanning electron microscope (SEM) images of graphene nuclei grown on Cu for different growth temperatures and times. Scale bar: 1 μ m. Figure from ⁸³.

2.3.5.2. Carbon precursors

Methane (CH₄) is the most common short chain hydrocarbon used as a carbon source in the CVD of graphene. Unsaturated hydrocarbon such as acetylene (C₂H₂) have been

used as a carbon source and is found to reduce the minimum growth temperature required for graphene down to 650 °C, since C_2H_2 has a lower decomposition temperature than methane⁹². Furthermore, Petera et al. , reported a CVD graphene on Ni substrate at growth temperature below 600 °C by using ethylene (C_2H_4) as a precursor⁹³. Also toluene (C_7H_8) has been used as a liquid carbon source through a bubbler or evaporator for low pressure CVD, due to its low decomposition temperature (500-600 °C) and low toxicity compared to benzene (C_6H_6)^{94,95}. A recent breakthrough was reported by Ham et al., who successfully grew continuous graphene film on Cu using C_6H_6 as a precursor at temperature range 100-300 °C under atmospheric pressure. After 5 minutes growth time the SLG coverage was 100 %⁹⁶. Solid carbon sources have been used as well such as poly(methyl methacrylate) (PMMA)⁹⁷, graphite⁹⁸, food, insect parts and solid waste⁹⁹. The advantages of using solid carbon sources are the growth temperature can be lower (~ 800 °C), it is less expensive and safer compared with expensive flammable gases like CH_4 . Recently Ruoff et al. successfully grew graphene on Cu substrate with no precursor but only a trace of C from the vapour of the pump oil¹⁰⁰.

2.3.5.3. Growth Pressure

Growth pressure is 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. Graphene growth on Cu under low pressure shows a self-limiting monolayer of graphene, while at high pressure non-uniform multilayers form¹⁰¹. 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 (vacuum) 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 sublimate the metal which leads to lower nucleation density^{102,103}.

2.3.5.4. Role of Hydrogen

The reaction mechanism of graphene growth using CVD method tends to be more complicated if the role of hydrogen (H_2) is taken into account. Libo et al. found that using CH_4 alone without H_2 gave good results and the graphene quality decreased with increasing H_2 partial pressure¹⁰⁴. Maria et al. proposed that the dissociative chemisorption of H_2 and dehydrogenation of CH_4 compete on available sites on the catalyst (Ni or Cu) which dampens graphene growth¹⁰⁵. Moreover, Yi Zhang et al. suggested that etching graphene with H_2 has a strong effect at different temperature, which can clean out the surface from graphene through reversing the growth process and forming hydrocarbon radicals (Figure 2.16)¹⁰⁶.

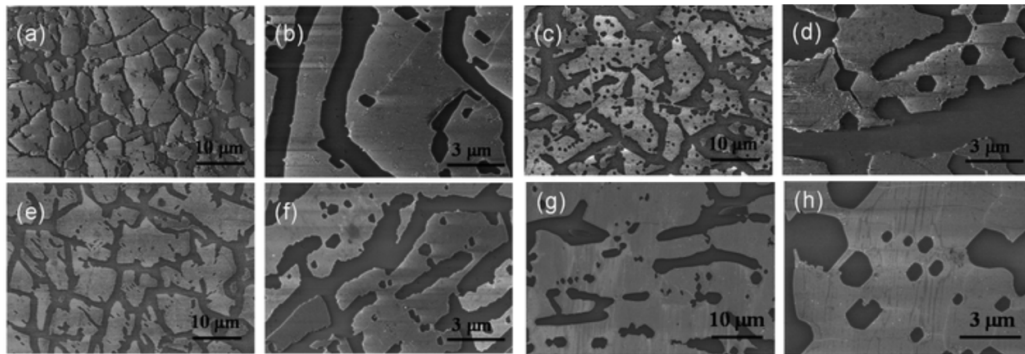


Figure 2. 16. SEM images of graphene/ Si/SiO₂ etched by hydrogen at different temperatures: (a and b) 700 °C; (c and d) 800 °C; (e and f) 900 °C; (g and h) 1000 °C. Figure from¹⁰⁶

On the other hand, Vlassiounk proposed that the presence of H_2 is very important for graphene growth since it facilitates the required methyl (CH_3) radical formation, which is considered a necessary step in the graphene reaction path. Moreover, graphene

growth under high H_2 partial pressure leads to well-defined hexagonal islands and this is because the hydrogen removes the unstable graphene edges, while under a moderate partial pressure the graphene has irregular islands shapes (Figure 2.17) ¹⁰⁷. Hydrogen shows a different role in the mechanism of graphene growth on Cu and Ni because the solubility of H in Cu and Ni is different. The diffusion coefficient of hydrogen in Ni is lower than in Cu ($2 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and $5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ for Ni and Cu respectively) ¹⁰⁸.

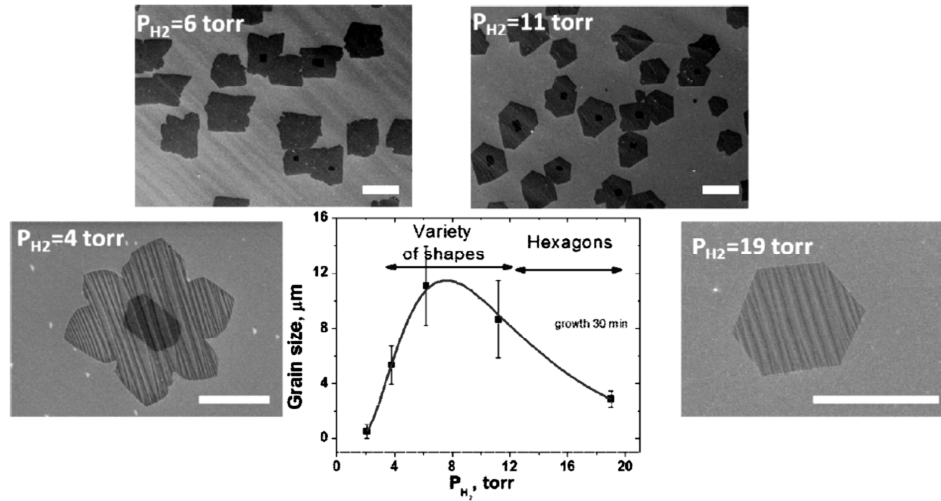


Figure 2. 17. Influence of hydrogen partial pressure on graphene average size grow at atmospheric pressure CVD on Cu foil at 1000 °C and 30 minutes growth time. The SEM images shows the difference in grain size with correspondence hydrogen partial pressure, increasing hydrogen partial pressure is critical to control the grain shape. Scales bars are 10 μm (top two images) and 3 μm (bottom two images). Figure from ¹⁰⁷.

Therefore, hydrogen recombines and desorbs from the Ni surface very fast, which is not the same behaviour with Cu according to equation:



The (s) indicates the free site on the metal surface, due to this there are always free sites on the Ni surface to decompose hydrocarbon and liberate C atoms which diffuse in bulk metal ¹⁰⁵.

2.3.5.5. Substrate

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 ¹⁰⁹ (Figure 2.18). Catalyst materials are either homogeneous, where catalyst and reactant are of the same phase (all solids or liquids), or heterogeneous, when catalyst and reactants are in a different phase. A catalytic CVD of graphene process is a heterogeneous system because the catalyst (metal substrate) is solid and the mixture is gas.

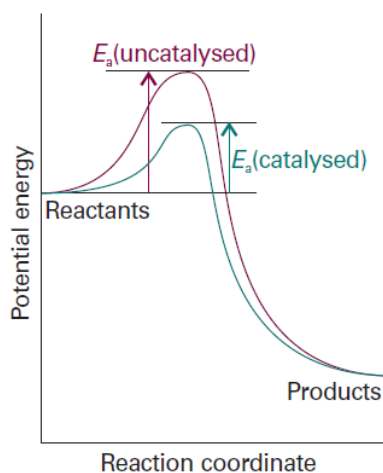


Figure 2. 18. Schematic diagram shows the energy profile difference between catalytic and non-catalytic reaction ¹⁰⁹.

There are factors which determine the suitability of different metal for use as a substrate for CVD of graphene. Since the graphene need to be transfer for its metal substrate by etching away the metal, the relative cost of that metal substrate become important from an industrial perspective (Cu is much cheaper than Pt). The other consideration is the catalytic activity of the substrate toward decomposition of hydrocarbon to produce active carbon radicals (C_xH_y). This is an important step in lowering the activation energy of cracking the hydrocarbon gases and prevents the growth being run under

snowing conditions. For instance, by using platinum as a catalytic substrate for CVD graphene, the growth temperature is lowered to 750 °C due to the strong catalytic activity to decompose methane¹¹⁰. In contrast, CVD of graphene on Cu requires a high growth temperature (1000-1040 °C) close to the melting point of Cu (1084 °C) due to the poor catalytic activity of Cu. Carbon solubility is also a vital factor that controls the graphene growth on metals; in fact, a graphene growth mechanism depends primarily on the carbon solubility. For example, Cu has low carbon solubility (0.001-0.008 wt. % at 1084 °C) plus low activity toward hydrocarbon decomposition. Therefore, graphene grows on Cu mainly due to the surface reaction which normally gives SLG. However, the solubility of carbon in Ni is considerably higher (~0.183-0.25 wt.%) which results in FLG graphene growth by segregation/ precipitation of carbon during the cooling stage¹¹¹.

2.3.6. Mechanism of CVD graphene growth

In general, the mechanism of graphene growth on transition metals includes two steps. The first step is the dissolution of the carbon source into the metal, and the second step is the segregation of carbon atoms during cooling to form graphene by precipitation¹⁰² (Figure 2.19). Segregation is heterogeneity in the composition, which corresponds to one phase in the phase diagram. On the other hand, precipitation shows inhomogeneity as a result of equilibrium phase separation. Blakely et al. studied first the segregation of graphene on the Ni surface; they found that monolayer graphene forms as the first step by segregation, followed by excessive precipitation leading to graphite formation¹¹².

The proposed mechanism of graphene growth over Cu and Ni starts by the chemisorption of the carbon source (hydrocarbon usually methane) on the transition metal surface⁷⁴. The empty d-shell in the transition metal's electronic structure

encourages the chemisorption of hydrocarbon on the metal surface which is ready to accept an electron. Following that, the dissociation of the hydrocarbon occurs by dehydrogenation to liberate carbon adatoms which will ultimately diffuse into the bulk metal. When the concentration of carbon atoms reaches a threshold for nucleation (the case with a Cu substrate), or during the cooling process (the case with a Ni substrate where the solubility of carbon in Ni decreases), the graphene precipitation/segregation occurs (Figure 2.19). The diffusion of carbon atoms out of the bulk metal does not stop until it reaches the equilibrium condition, even if the gas phase carbon source is turned off ¹⁰².

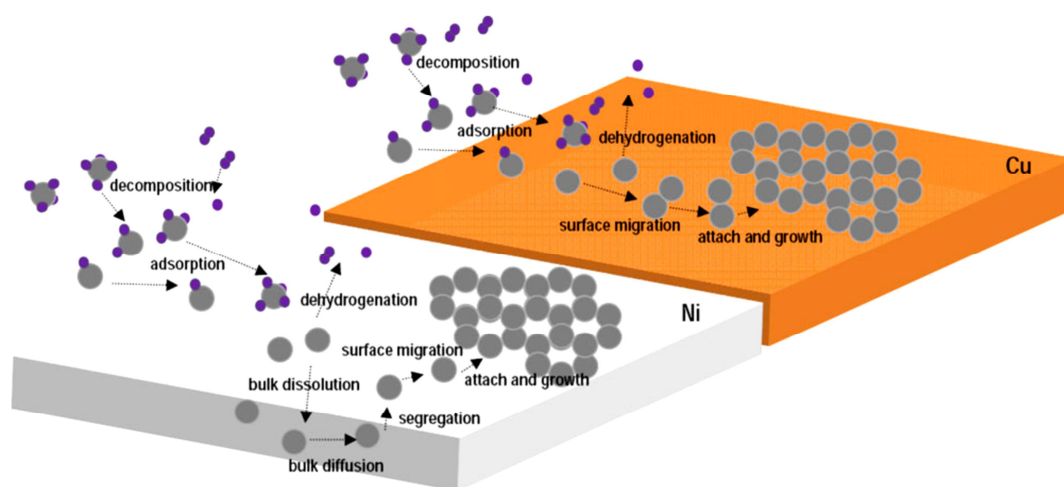


Figure 2. 19. Cartoon illustrates mechanisms of graphene growth by CVD technique on Cu and Ni. Hydrocarbon gas (methane) adsorbs on the metal surface and dehydrogenates to liberate carbon atoms which form graphene lattice either by surface isothermal growth (CVD of graphene on Cu), or carbon atoms diffuse into the metal bulk and segregate upon cooling to form graphene (CVD of graphene on Ni). Figure from ⁹⁴.

The solubility of carbon in metal substrates plays an important role in determining which mechanism (precipitation/segregation) follows. For Cu, with a very low solubility of carbon, graphene forms after hydrocarbon dissociation and no further graphene will form if the carbon source is turned off ¹¹³. The story with Ni is different; since the solubility of carbon in Ni is high, the path of graphene deposition starts with

chemisorption, dissociation, diffusion of carbon into the bulk metal and finally diffuses out during cooling to form graphene on the surface.

Graphene has incredible properties, which makes it promising for a number of electronic applications such as touch screens, smart windows, flexible displays, solar cells and supercapacitors ¹¹⁴. However, to unlock outstanding graphene properties, an appropriate synthesis method required. CVD is the most suitable route to produce graphene regarding large areas, quality, and cost. Nevertheless, there are still challenges which need to be solved, such as controlling the number of layers and graphene grain size. Therefore, studying the CVD graphene growth mechanism is essential to improve and control graphene film quality. Ruoff et al. ¹¹¹ used isotopic labelling of the C precursor to study the CVD growth of graphene mechanism. Their experimental work included introducing normal methane ($^{12}\text{CH}_4$) and $^{13}\text{CH}_4$ to the growth chamber in a sequence that took the advantage of the fact that each C isotope has different Raman modes due to the mass difference between ^{13}C and ^{12}C . They concluded that the CVD graphene growth mechanism is either surface adsorption for metals with low C solubility such as in Cu, or segregation, which is accompany to high C solubility metals like Ni. In this work, the transition between the two mechanisms (surface adsorption and segregation) is investigated. The Cu-Ni alloys compositions ensure covering the C solubility range between pure Cu (low C solubility) and pure Ni (high C solubility); therefore it been used as a catalytic substrate model.

3. Methodology

3.1. Introduction

This chapter describe in detail the CVD system used in this study. The characterization techniques used to examine the grown graphene films are also presented with their physical principles outlined. Two main techniques are used, Raman spectroscopy and scanning electron microscopy (SEM) to characterise the carbon thin films grown on the catalytic surface. Raman is a quick and accurate technique for the identification of carbon allotropes, coupled with SEM to study the morphology of the films a better understanding of their properties can be achieved. Glow Discharge Optical Emission Spectroscopy (GDOES) was also used as a complementary analytical technique; it is typically used to depth profile elements with interest in this study (C, Ni and Cu).

3.2. CVD system

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 (Figure 3.1)¹¹⁵

However, all different types of CVD must have four basic units:

- **Precursor delivery unit:** this unit supplies precursor materials to the reaction chamber in a controlled way after mixing with carrier and diluent gases.
- **Energy source:** this provides the energy, usually heat, required to the reaction vessel to start the precursor's reaction, and also to maintain a given temperature level during the reaction time.

- **Exhaust gas unit:** this removes the by-products and unused gases from the reaction chamber via pipelines and pumps.
- **Control unit:** this includes Mass Flow Controllers (MFC) which keep the volume rate of flowing gases constant through the process, and also include pressure gauges and temperature controllers.

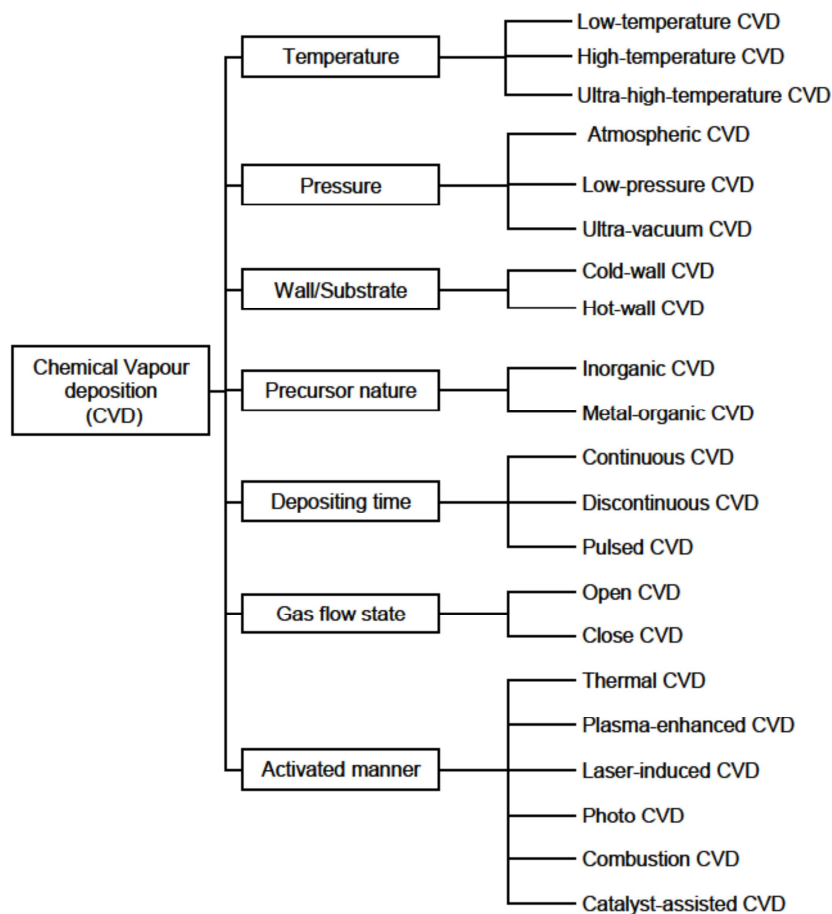


Figure 3. 1. The seven main types of CVD methods classified based on processing parameters¹¹⁵.

The CVD system used in this study is an open flow hot wall homemade system which was designed to meet the four basic requirements of the CVD process.

The gas delivery unit has three gas lines (Figure 3.2), Methane (CH₄), Hydrogen (H₂) and Argon (Ar) which are all supplied at a high purity (99.95%) (BOC, Guilford, UK). Methane is a carbon source for CVD graphene, which is consider a saturated, highly

stable hydrocarbon; it has a low C-H bond energy ($\sim 410 \text{ kJ mol}^{-1}$)⁹⁴. One role of hydrogen is to remove any native oxides on the metal surface during the annealing process and to dilute methane, which certainly play a role in CVD graphene. Argon is usually used to increase background pressure during growth and is also consider a diluent gas. For safety, the gases were provided to the CVD system from a central gas supply, and gases are delivered to the laboratory by medical grade stainless steel pipes. Regulators, at the end of each pipe in the laboratory, control the pressure of the gas and ensure to feed the system at constant pressure (1 bar).

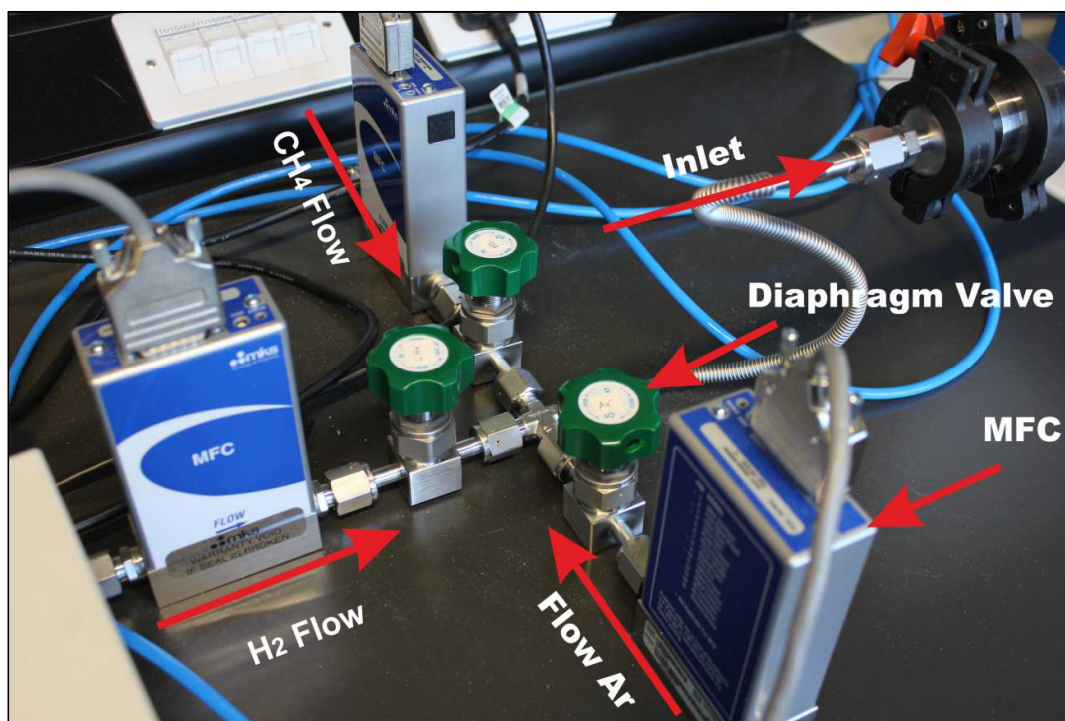


Figure 3. 2. CVD mixing-delivery unit. Nylon pipes (blue) deliver the gases to MFCs, which control the flow rate. The red arrow shows the flow direction for assigned gas through the diaphragm valve which is connected to one end to MFC and four-way pies in the other. The flowing gases mix in the four-way connector and enter reaction chamber through inlet end.

The CVD system is connected to a pressure regulator by Nylon pipes. The mixing-delivery unit consists of MFCs (MKS Instruments 1179A/B), one for each gas, which controls the pre-set volumetric flow rate. Each MFC was calibrated for a specific gas, so

each gas has its manufacture designated and calibrated MFC. Each gas line is isolated from the other gas lines by a diaphragm valve. The gases, each with its designated volumetric flow rate, were mixed in a four-way connector, one way for each gas and the fourth one is for the inlet line which is a flexible 6mm in diameter stainless steel pipe (Figure 3.2). A three-zone clam-shell furnace (PSC 12/90/600H Lenton Eurotherm) provides energy to start the growth reactions. The furnace 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 2.2 cm inner diameter, and 0.3 cm wall thickness (Figure 3.3).

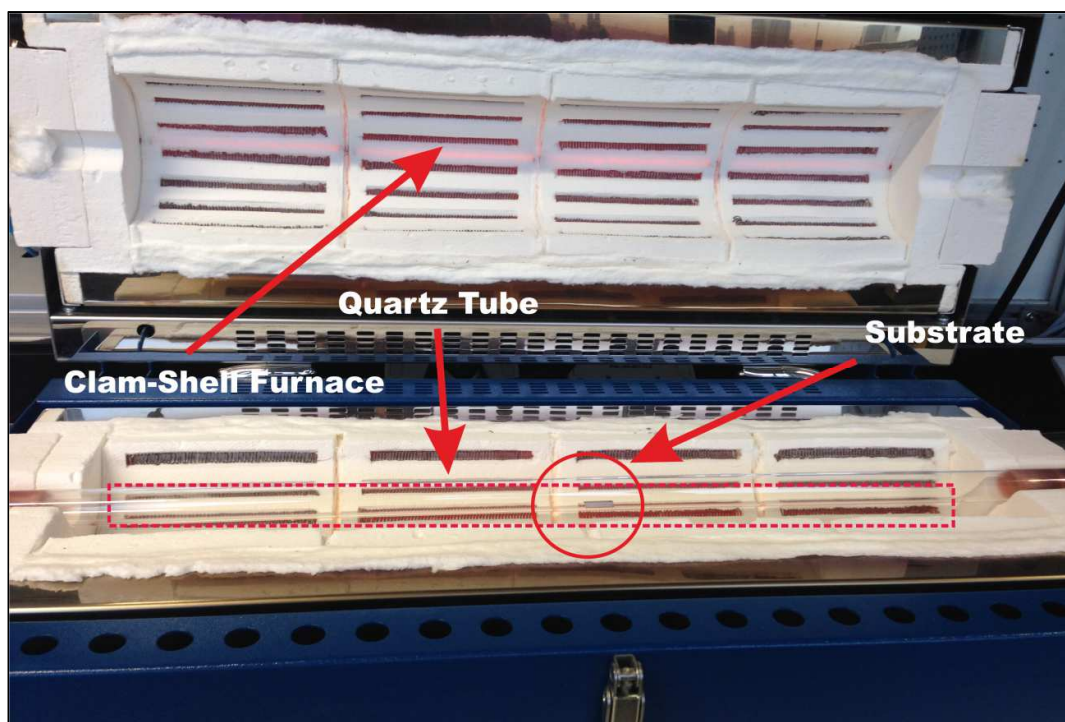


Figure 3. 3. Reaction chamber (25 mm quartz tube) loaded with a metal substrate fitted inside a clam-shell furnace (energy source).

The reactant gases are extracted from the reaction chamber through a two-stage rotary vane pump (Edwards RV12). The pump ultimate pressure is 2×10^{-3} mbar and it is connected to the chamber outlet via a flexible stainless steel tube to minimize the effect

of pump vibration on the reactor. A capacitance pressure gauge is fitted between the outlet end and the pump to monitor the reactor pressure during the CVD process. The CVD rig is connected and disconnected from the pump by a manual in-line lever operation isolation valve. Both reaction chamber ends are connected to the inlet and outlet by stainless steel fittings and O-rings to maintain a good vacuum during the process (Figure 3.4).

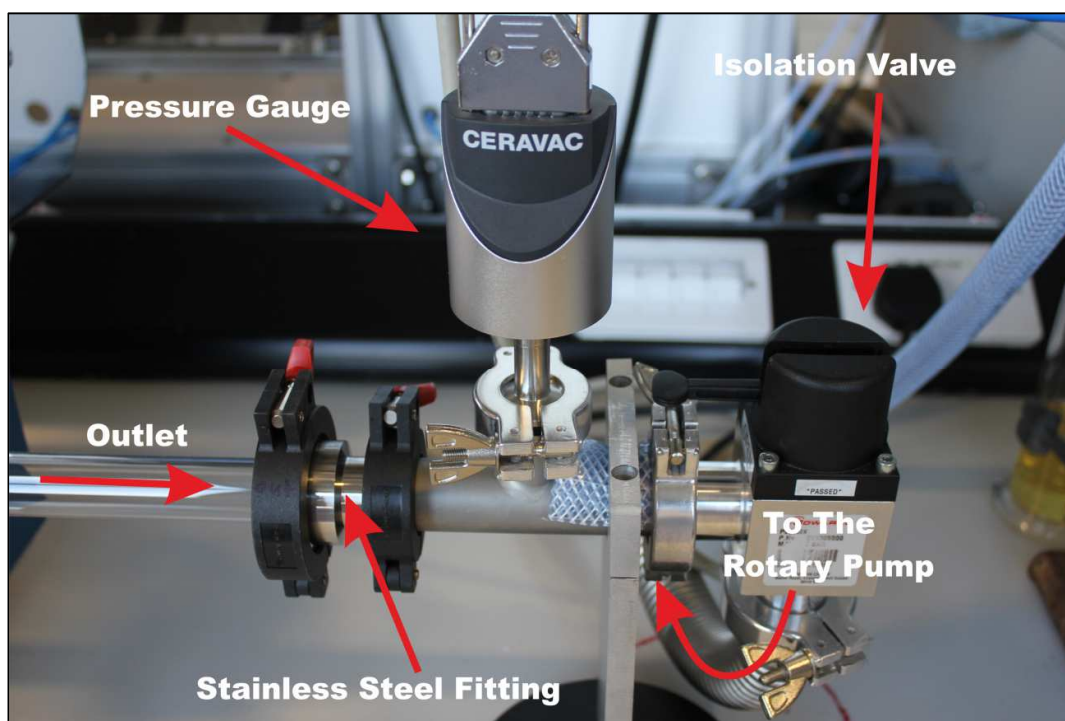


Figure 3. 4. Exhaust unit, which removes by-product gases out from the outlet end. Quartz tube connected to exhaust unite via stainless steel fitting. Isolation valve mounted between the reaction chamber and rotary pump. Pressure gauge located in the way between outlet and isolation valve to monitor chamber pressure during the growth process.

3.3. Growth procedure

In this study, five different concentrations of copper-nickel alloy were used as catalytic substrates for CVD graphene growth. The substrates have their composition tabulated in Table 3.1. All the substrates have the same thickness 500 μ m and were obtained from

two different suppliers, Goodfellow (Cambridge, UK) and Alfa Aesar (Haverhill, MA, USA) respectively.

Table 3. 1. Substrate specifications used in this work.

Substrate	Purity	Typical Analysis (ppm)	Supplier	Note
Nickel	99.98%	Co 8, Cr 8, Cu 10, Fe 10, Mg 10, Mn 10, Si 8, Ti 10, C 70, S 10	Goodfellow	Annealed
Copper	99.99%	Ag 70, Al 1, Bi 1, Ca 1, Cr <1, Fe 2, Mg 1, Mn <1, Na <1, Ni 2, Pb 2, Si 2, Sn 1	Goodfellow	As rolled
Cu70/Ni30	-	Cu 67.3%, Ni 31.0%, Mn 1.0%, Fe 0.7%.	Goodfellow	As rolled
Cu55/Ni45	-	Fe 2500, Mn 7500, Ni 45%, Cu balance	Goodfellow	As rolled
Cu33/Ni67	-	-	Alfa Aesar	

The advantage of using thick substrate foil is it's easily of handling especially under vacuum when changing pressure due to the introduction of process gases (H_2 and CH_4) because thin foils were displaced or swept away by sudden gas flows caused by a pressure change. In addition, thin foils might bend or loss their flatness during the loading and unloading process. The foil substrate samples, of dimensions $\sim 1\text{cm} \times 1\text{cm}$, were cut from a larger sheet with shears, and one corner were clipped to identify the top and bottom face.

The CVD growth process sequence is represented in Figure 3.5. The pump is switched on first before starting the process, and it is recommended to leave it running for fifteen minutes to allow the oil to warm up for better and constant efficiency. The metal substrate is handled with a stainless steel tweezer and loaded in the reaction chamber, then pushed in further with a polymer stick to the central position in the quartz tube. The chamber is then sealed and connected to the rotary pump by opening the isolation valve gradually.

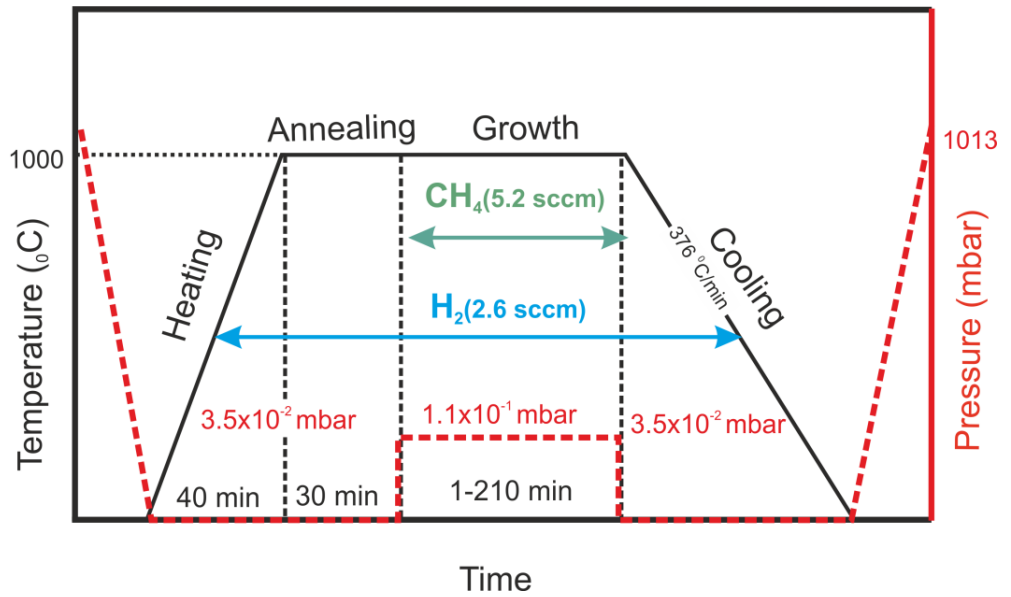


Figure 3. 5. Schematic illustrates the experimental procedure of CVD growth process.

The system is then evacuated until it reaches the ultimate pressure (2×10^{-3} mbar) which confirms that the vacuum system is operating appropriately and there is no leak in the system. The hydrogen flow is introduced first for annealing purposes at a volumetric flow rate of 2.6 sccm. Once the hydrogen starts to flow, the system pressure jumps to 3.5×10^{-2} mbar (Figure 3.5). The next step is to switch on the furnace at a heating rate of $25\text{ }^{\circ}\text{C}/\text{min}$; after 40 minutes it reaches the target annealing temperature of $1000\text{ }^{\circ}\text{C}$. The sample is then annealed under flowing H_2 for 30 min at $1000\text{ }^{\circ}\text{C}$. Annealing of the substrate is considered a vital process in CVD graphene growth since it reduces the native surface oxide and enlarges the grain size¹⁰⁷.

The growth process begins as soon as methane is fed into the reaction chamber with the reactor pressure increase to 0.1 mbar because of the presence of a flow of methane at 5.2 sccm. The CH_4 : H_2 ratio is 2:1 by volume which gives an overall carbon-to-hydrogen atomic ratio (R_{CH}) of 0.2. These process conditions have previously shown good results for graphene growth on a copper foil with the same CVD rig as used in this work¹¹⁶, so it has been adopted as the standard growth conditions used in this work

unless otherwise stated. The appropriate growth time varies based on the substrate composition, with an increase in the nickel content requiring increases in the growth time. The growth stage finishes when the methane flow is stopped and the substrate is allowed to cool down either naturally (slow cooling) at a rate of $27\text{ }^{\circ}\text{C}/\text{min}$ or by opening the shell furnace and letting the furnace to cool down (fast cooling) at a rate $367\text{ }^{\circ}\text{C}/\text{min}$. 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. When the system reaches room temperature, the hydrogen flow is stopped, and the system is isolated from the pump by closing the isolation valve. The introducing of argon flow increases the chamber pressure and until it reaches atmospheric pressure (1013.2 mbar) then the chamber is opened and the sample unloaded for characterisation.

CVD is a vapour transfer process, which is atomistic in nature, *i.e.* the deposition species are either atoms or small molecules or sometimes the combination of both. Hence the process is susceptible to any changes in the reactor gas atmosphere. Alterations of the feedstock purity, substrate composition and even the gas pipelines may give unexpected results. Figure 3.6 shows one of those cases when the gas pipelines became contaminated during the work on this project for unknown reasons. The contaminant substance swept by gas flow stream in the lines and enters the MFCs and mixed with reactive gases and as a result, the graphene growth reaction pathway was diverted (Figure 3.6(a)). Figure 3.6(b) shows the normal deposition inside the quartz tube after consecutive runs. The growth temperature ($1000\text{ }^{\circ}\text{C}$) is near the melting point of the copper substrate and together with the low growth pressure and high vapour pressure of solid copper leads to significant metal evaporation, and deposition on the inside surface of both quartz tube ends. Furthermore, after several growth cycles, the inside of the outlet surface at the end of the quartz tube is decorated with carbon (Figure 3.6(b)), which is a normal observation for low pressure CVD

growth¹¹⁷. Therefore, inspection of the quartz tube ends (especially the outlet end) gives a good indication if the gas chemistry is not as it is meant to be, Figure 3.6 (c) and (d).

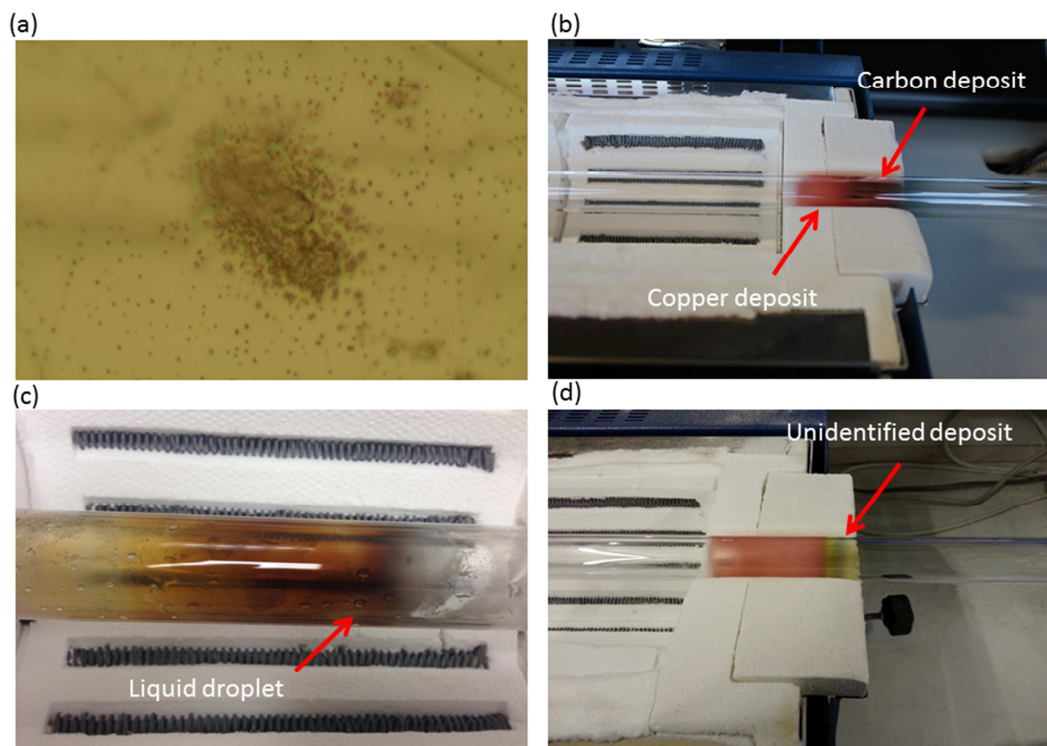


Figure 3. 6. (a) Optical spectroscopy image of the contaminated copper substrate. (b) Outlet end of the quartz tube decorated with copper and carbon from continuous CVD use. (c) Contamination during atmospheric pressure CVD (APCVD) growth, it is evident from figure formation of some unknown liquid by-product. (d) One of the cases shows a yellow residue from liquid hydrocarbon previous APCVD run. All presented cases CVD graphene fail to grow.

3.4. Film Characterization

Graphitic films can be analysed without transfer to a dielectric substrate, which is a good way to investigate the effect of the substrate and growth conditions on the deposited film. Raman spectroscopy and SEM can be used to provide sufficient understanding of the number of graphene layers, stacking order, electronic structure, and surface coverage. GDOES was also used for elements depth profiling, which delivered necessary information regarding the substrate bulk role.

3.4.1. Raman Spectroscopy

Raman spectroscopy is one of the main characterisation techniques used to probe both the electronic and structural characteristics of carbon allotropes.

The Raman Effect, named after the discoverer Sir C.V.Raman ¹¹⁸, is an inelastic scattering of photon by vibrational phonon of the sample ¹¹⁹. When the photon and the material interact, the photon can lose part of its energy $\hbar\omega_{sc}$ (where $\hbar$ is Plank constant and ω_{sc} is the photon frequency) by transferring it to the sample and creating a phonon of energy $\hbar\Omega$ (Ω is the vibration frequency); this process called Stokes (S). However, if the material transfers energy to the absorbed photon *i.e.* the emitted photon has higher energy than the absorbed photon, which happens when the photon absorbs phonon, then the process is called Anti-Stokes (AS) ¹¹⁸. Raman scattering provides a good tool to probe the properties of materials, since each material has unique vibrational modes. The phonon dispersion of SLG graphene includes six branches: three acoustic (A) and three optic (O) of which one optic (O) and one acoustic (A) vibrating out-of-plane (o), while the remaining two optic and two acoustic are vibrating in-plane (i) which are either longitudinal (L) or transvers (T) photon modes (Figure 3.7) ¹²⁰.

Graphene spectra under Raman spectroscopy mostly show three characteristic peaks: D, G and 2D, at around 1350 cm^{-1} , 1580 cm^{-1} and 2700 cm^{-1} respectively ¹²¹. The G band refers to the doubly-degenerated optical phonons (iTO and LO) at the Brillouin zone centre Γ and it is coming from the first order Raman scattering process. However, D band originate from double-resonance processes, involving degenerating one iTO and one defect near the K point. On other hand, 2D band coms from a double-resonance process and is generated from two iTO phono modes (Figure 3.8).

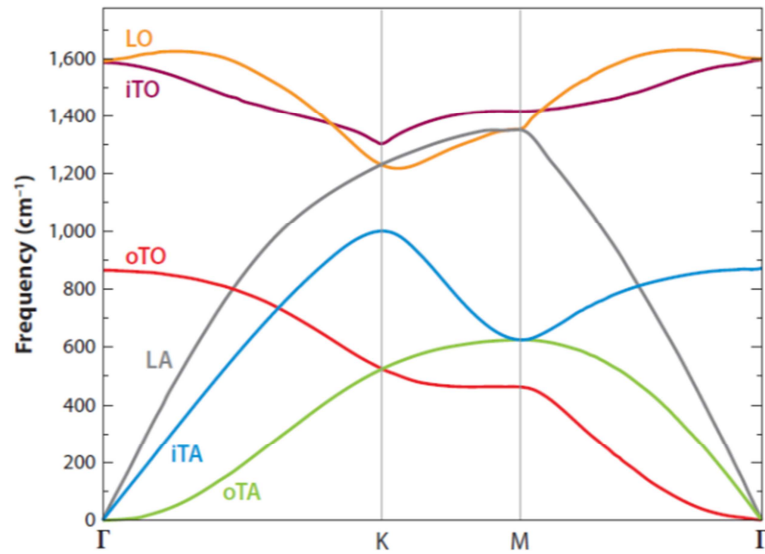


Figure 3. 7. Phonon dispersion relation of graphene showing the iLO, iTO, oTO, iLA, iTA and oTA phonon branches. Figure from ¹²⁰.

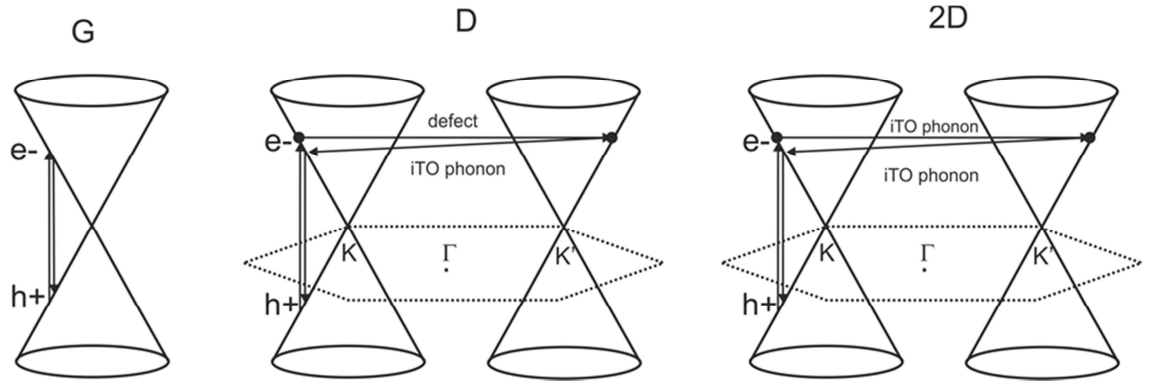


Figure 3. 8. First-order Raman process (G band), one-phonon second order double- resonance Raman process (D band) and two phonons second order double resonance Raman process (2D band). Adopted from ¹²².

Raman spectroscopy is a very accurate technique for characterizing graphene atomic structure and electronic properties, because it's zero bandgap makes all the incident wavelength resonance. The number of graphene layers can be determined by Raman spectroscopy because G band intensity increases with increasing the number of graphene layers, due to more carbon atoms taking part in the vibration mode ¹²³. Moreover, defects in graphene structure are also possible to detect by Raman spectroscopy, because D band is activated by defect ¹²². The use of Raman technique in

graphene research has been extended to include graphene stacking order¹²⁴, strain detection in graphene^{125,126} and graphene functional groups^{127,128}.

In this work, coverage and uniformity of graphitic films derived from CH₄-H₂ gas mixtures were acquired using a LabRAM HR Evolution Raman system (Jobin Yvon) with a 488nm wavelength laser and 50 x, normal working distance, objective lens. The scan covers a range from 1200 cm⁻¹ to 3000 cm⁻¹ in which all the graphene characteristic peaks lie. The laser power was set at 70% with a neutral-density filter (ND) 10% and the acquisition time was 30 s. All the collected Raman spectra were analysed and fitted by LabSpec 6-Horiba Scientific software. The G to 2D peak intensity map ratio (I_{2D}/I_G) in conjunction with a 2D peak full width at half maximum (FWHM) and shape was used to determine the number of graphene layers present. Range was set for I_{2D}/I_G from 1.4 to 0.7 and 2D FWHM from 45 to 60 cm⁻¹ for BLG. I_{2D}/I_G higher than 1.4 and FWHM of 2D peak less than 45cm⁻¹ was considered as indicating a monolayer or single layer graphene (SLG), while I_{2D}/I_G less than 0.7 and a 2D peak FWHM of 60 cm⁻¹ was considered as indicating a few layer (FLG)^{129,130}.

3.4.2. Scanning electron microscopy (SEM)

The basic components for any SEM are an electron gun system to generate accelerated electrons, an electron probe which is a lens system and a detector to collect the electrons scattered from the specimen. When electron beam strikes a specimen it will interact with its surface and scatter from the near-surface bulk. The scattering volume takes a pear-shape which is known as the interaction volume. As a result of this process, different signals are emitted, of which the most important are backscattered electron (BSE), low energy secondary electrons (SE) and characteristic X-rays (Figure 3.9)¹³¹. Electron energy, specimen atomic number and density of the specimen determine the

scattering length. The interaction between incoming fast electrons and specimen atoms lead to elastic and inelastic electron scattering. Elastic scattering occurs when the electron interacts with the atomic nucleus with no energy transfer, while when incoming energetic electrons interact with the atomic electrons, inelastic scattering results with energy transfer. Forward scattering (inelastic scattering) is most dominant in these kinds of interactions with $< 90^\circ$ divergence angle, unlike elastically backscattered electrons with a divergence angle $> 90^\circ$. Backscattered electrons (elastic scattering) have high kinetic energy, which enables them to leave the specimen towards the vacuum which gives rise to the BSE signal. Due to their low energy SEs in the bulk are absorbed quickly by the specimen and only the electrons near the surface can be emitted. Therefore the SEM image generated when a specimen surface is scanned with a focused electron beam represents both SE and BSE signals at each surface point (pixel). The intensity of the generated electron signals is very sensitive to specimen composition and topography. Scanning electron microscopy provides a high resolution image with high magnification, it is easy to use by trained users and it does not require special sample preparation, merely mounting the sample on a conductive stub is usually sufficient. SEM is usually included in any CVD graphene study to measure the graphene grain size, graphene coverage and it gives valuable information about the substrate topography changes after growth. CVD graphene SEM images show a different contrast with different numbers of graphene layers (low contrast indicates few graphene layers). All the SEM images included in this work, were acquired with an XL-30 FEG SEM (FEI, Eindhoven, Netherlands) with a spot size of $3\mu\text{m}$, a working distance of 7.6 mm and an accelerating voltage of 8 kV.

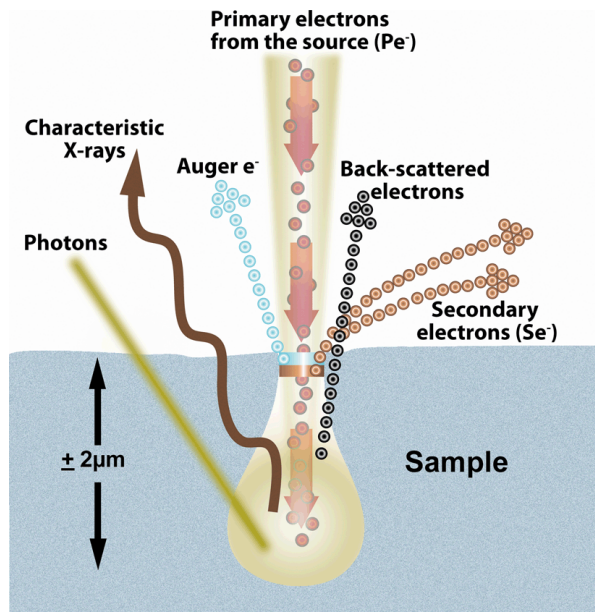
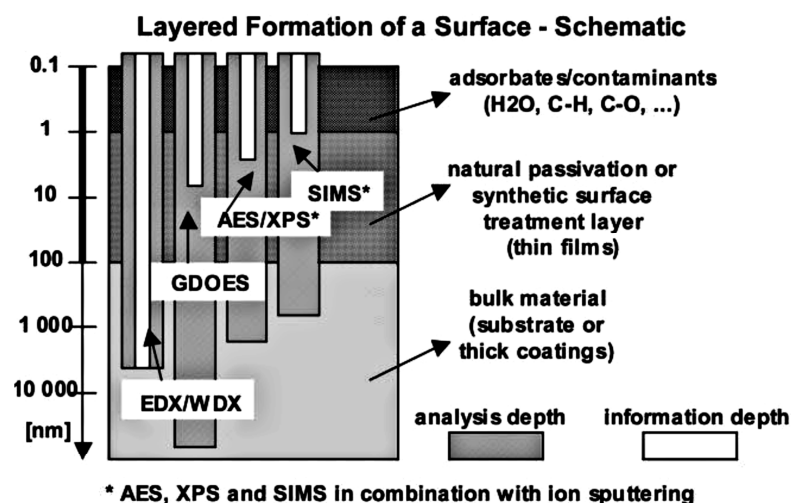


Figure 3. 9. Interacting of the incident electron beam with the sample, results in different kinds of emissions, low-energy secondary electrons (SE), back-scattered electrons (BSEs), light emission, characteristic X-ray, and others as shown. Figure from reference ¹³¹.

3.4.3. Glow discharge optical emission spectroscopy (GDOES)

The use of GDOES for bulk analysis of metals started at the 1960s following Grimm efficient dc discharge cell ¹³². The application of GDOES was extended after the development of a radio frequency (rf) mode for the technique, which makes analysis of nonconductive materials possible by GDOES. Among the other techniques, GDOES has advantages of high sensitivity, speed of analysis and easy use¹³³. It can be used for both thin film analysis, and it can also provide bulk depth information down to > 10000 nm (Figure 3.10)¹³⁴.



Acronym	Technique	Information depth/nm
SIMS	Secondary Ion Mass Spectrometry	1
AES	Auger Electron Spectroscopy	2
XPS	X-ray Photoelectron Spectroscopy	2
GD-OES	Glow Discharge Optical Emission Spectrometry	6
EDX	Energy Dispersive X-ray Analysis	5000
WDX	Wavelength Dispersive X-ray Analysis	5000

Figure 3. 10. Schematic drawing showing the surface layered formation with the depth analysis techniques. Figure from¹³⁴.

In glow discharge, two electrodes are placed in a space filled with noble gas (usually Ar) and a voltage is applied to generate a plasma¹³³. The plasma is generated under low pressure (ranging from 100 to 1000 pa), and it is electrically neutral, however, it is not homogeneous. Gas positive ions move under the influence of an electric field toward the cathode (Sample under test) and bombardment of the surface causing sputtering. All the particles (ions, electrons, gas atoms and sputtered atoms) undergo different types of collisions (Figure 3.11). Full Details of these collisions is unclear, which make understanding the glow discharge plasma difficult. When sputtered atoms leave the sample surface, they quickly slow down to thermal speeds due to collision with gas atoms. Therefore, they either go back to the surface or sputter the sample by itself. The sputtered atoms can get excited as a result of a collision with electrons or metastable gas atoms. The excited state of the cathode atoms does not last for a long time because they

lose energy by emitting characteristic wavelength photons corresponding to the elements present in the cathode. Therefore, depth composition information can be obtained by sputtering layer-by-layer from the target material and the characteristic wavelengths emitted are recorded¹³⁵.

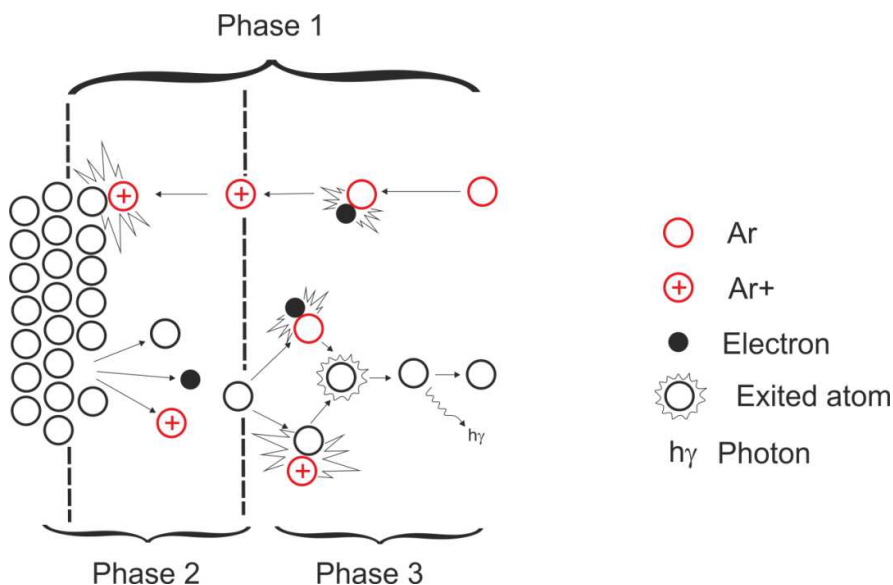


Figure 3. 11. Glow discharge processes. Phase I, plasma generation and sample surface bombardment. Phase II, sample surface sputtering. Phase III, emitting of characteristic wavelength by the excited and de-excited process. Adopted from¹³⁵.

The elements depth profile of the CVD graphene performed by HORIBA Jobin Yvon (Kyoto, Japan) RF GDOES. The test specimen does not require any pre-treatment except that the size should be $>1.5 \text{ cm}^2$ and flat to be able to be held in a designated position under vacuum. Cu, Ni and C compositions were depth profiled with emission lines 325, 341 and 156 respectively. Argon flashing time is 30 s and sputtering time as well, so the whole run for one sample takes 1minute. A result curve shows sputtering time (seconds) vs intensity (volt), which is possible to convert it to concentration vs depth, however, for accurate quantitative composition data, the GDOES depth profiler

needs to be calibrated for each of the three elements of interest which were beyond the scope of this work.

4. CVD of graphene on pure metals

4.1. Introduction

The interest in graphite synthesis stretches back a time¹³⁶. The first significant work focused on attempts to transform amorphous carbon to graphite. Some researchers proposed that high temperature (3000 °C-3500 °C)¹³⁷ be enough to convert amorphous carbon to crystalline graphite. While others thought just heat is not sufficient alone. However, this was all theoretical ideas with no experimental support¹³⁸. Acheson (U.S. Patent, 568,323, Sept.29, 1896) successfully converted cheap and common carbon materials such as coke or mineral coal to graphite, but his initial work had a very low yield of graphite. However, by mixing carbon with 3% iron oxide, the yield of graphite produced increased. Acheson was unsure of the role of iron oxide in the improvement, but he assumed that it had a catalytic effect.

In a parallel study, Banerjee studied the formation of pyrolytic carbon (carbon material deposited from gaseous hydrocarbon compounds on suitable underlying substrates at temperatures ranging from 1000 K to 2500 K¹³⁹) by hydrocarbon gas decomposition over metallic surfaces compared with non-metallic surfaces. The results show the effect of substrate composition on the crystallinity of pyrolytic carbon films prepared on active catalysts such as Nickel and Iron¹⁴⁰. The recent interest in graphene research and the CVD growth of graphene film has led to a reappraisal of these early studies. Graphene can be simply grown by thermal decomposition of hydrocarbon gases on transition metals, including Ru¹⁴¹, Ir¹⁴², Fe¹⁴³, Pt¹⁴⁴, Ru¹⁴¹ Ni¹⁴⁵ and Cu¹⁴⁶. This chapter presents a study of the CVD growth of graphitic films on catalytic pure metal substrates of Cu and Ni.

4.2. Interaction of carbon with transition metals

The reactivity of transition metals toward carbon can be classified into three degrees of reaction intensity: weak (e.g. Cu, which is considered relatively inert to carbon), moderate (e.g. Ni, which can dissolve a substantial quantity of carbon into solid solution) and strong (e.g. Ti, which reacts strongly with C to form a stable carbide phase). The reactivity of transition metals with carbon is governed by their electronic structure. Overlapping of the transition metals *d*-orbitals with the *p*-orbital of carbon is the pathway for carbon-transition metal reactions. According to this, the number of electron vacancies in the *d*-orbital has a significant impact on transition metal reactivity. Metals with no *d*-orbital vacancies (e.g. Cu and Au) can only dissolve a negligible amount of carbon in their bulk structure, unlike the case of metals with available vacancies (e.g. Ti) that can react and form stable carbide with variable carbon/metal ratio (Figure 4.1) ¹⁴⁷.

The hypothetical mechanism for the growth of carbon allotropes by catalytic CVD is believed to start by adsorption of hydrocarbon chemical species at active free catalyst surface sites, with the reaction initiating by dissociation of hydrocarbon molecules to liberate carbon as a reaction product ¹⁴⁸. Metals with high reactivity to carbon (e.g. Ti) are considered to be poor catalysts for graphitic film deposition because it becomes deactivated in a short time by the formation of the metal carbide. The strong carbon-metal bond blocks free catalyst surface active sites and no more hydrocarbon species adsorption is possible ¹⁴⁹. Figure 4.1 shows the relative enthalpy of formation and carbon/metal ratio for the stable carbide phase as a function of the number of electrons in the *d*-orbital. Moving from left to right in the figure, carbon-metal reactivity decreases as is clear from the trend in carbide heat of formation. So far, the transition metals successfully used as substrates for CVD graphene growth are Ru, Ir, Pt, Ni, and Cu. Ru is a widely studied catalyst, because of its carbon solubility (0.34 at% at

1000 °C) which is between Cu (0.008 at %) and Ni (0.9 at%)¹⁰². Moreover, its single-crystalline hexagonal closet-packed (hcp) structure that forms after heating, ensures flatness and reduces graphene grain boundaries¹⁵⁰. The mechanism of graphene growth in Ru (0001) as proposed by McCarty group is the same as in Ni *i.e.* diffusion of the C adatoms to the bulk continues until reaching the supersaturation limit^{151,152}. The number of graphene layers can be controlled in Ru by manipulating the growth temperature, which in turn controls the C solubility¹⁵³. Ir has a 0.041 at% carbon solubility¹⁵⁰, which is useful for the self-limiting growth of SLG and BLG. However, due to the large difference in thermal expansion between Ir and graphene, (Ir contraction after cooling is 0.8%), the graphene produced is defected by wrinkles¹⁵⁴. The mechanism of CVD graphene growth on Ir (111) is similar to that of Ru(0001), which is limited by the diffusion of C from the metal bulk to the surface after reaching supersaturation concentration¹⁰². Unlike Ni, Ru, and Ir, the mechanism of CVD graphene on Pt is similar to that of Cu *i.e.* chemisorption growth, due to low C solubility in Pt (0.0043 at%)^{144,155}. All of the mentioned catalysts (Ru, Ir, Pt, Ni, and Cu) are characterized by low or moderate reaction intensity with carbon, which means they do not form carbides that make them suitable substrates for CVD graphene. However, Cu and Ni are most commonly used as a substrate for graphene growth, because of their cost and available grain size. In addition, both Cu and Ni can be readily removed from the graphene film through chemical etching. Figure 3.1 shows that the catalytic activity of Cu and Ni is dissimilar because they have a different electronic structure.

This explains the difference in carbon solubility values for Cu and Ni. According to Figure 4.2(a)-(b), which displays the phase diagram of Ni-C and Cu-C respectively, carbon solubility in Ni is higher than in Cu, and of 0.183 w% and 0.004 w% respectively.

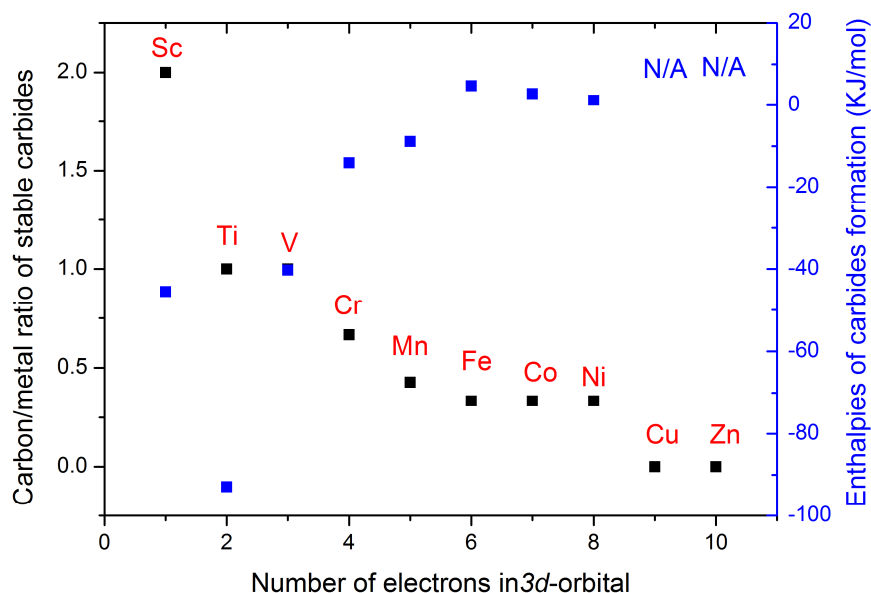


Figure 4. 1. Metal carbide enthalpies of formation¹⁵⁶ and carbon to metal ratio of the stable carbide¹⁴⁷ vs a number of electrons in the 3d-orbital for transition metals. Note N/A for Cu and Zn means they have no stable carbide phase.

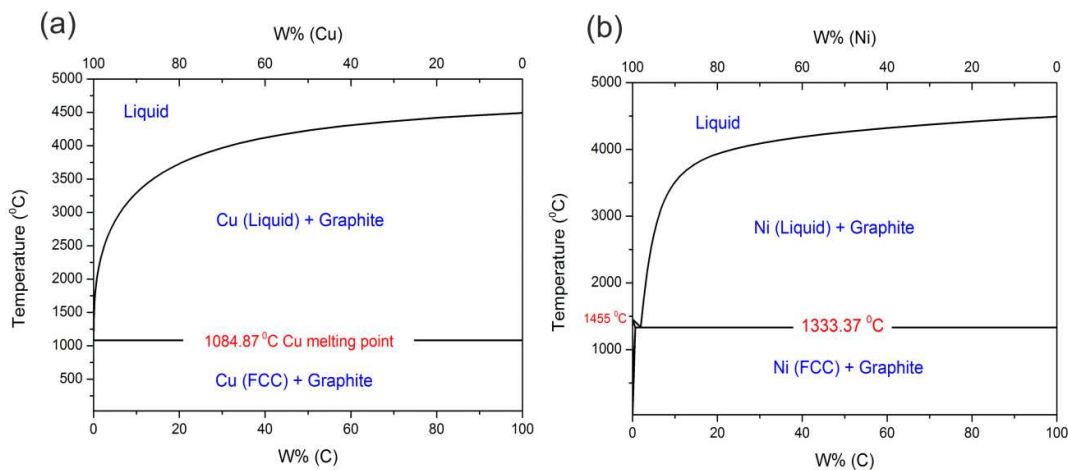


Figure 4. 2. Carbon –metal phase diagram calculated by Pandat¹⁵⁷. (a) Cu-C system. (b) Ni-C system.

4.3. CVD growth of graphene on Copper

Graphene films were grown on Cu substrates using the standard low pressure chemical vapour deposition (LPCVD) growth parameters described in methodology chapter (see Figure 3.5) unless otherwise stated. This CVD system was used for previous projects in

Manchester ¹¹⁶, in which case first experiments were used to reproduce these experiments using identical growth conditions including the same substrate.

Raman spectroscopy results from LPCVD grown graphene on 25 μ m thick Cu substrates are shown in Figure 4.3. Raman map of the peak intensity ratios I_{2D}/I_G (Figure 4.3(a)) in conjunction with a map of the 2D peak full-width half maximum intensity (FWHM) map (Figure 4.3(b)) indicates the presence of a single graphitic layer covering the Cu foil surface. The I_{2D}/I_G range is $\sim 1.5 - 2$ and the 2D FWHM is in the range $\sim 29 - 37$, which is in good agreement with the reported Raman fingerprint for CVD single layer graphene ¹³⁰. The Raman spectrum (Figure 4.3(c)) reflects the features found with single layer graphene, however, the 2D band position is $\sim 2713 \text{ cm}^{-1}$ with $\sim 13 \text{ cm}^{-1}$ blue shift compared with the spectrum found from graphene films transferred film onto SiO₂/Si substrate, which is 2700 cm^{-1} for the 488 nm Raman laser. The difference between the as-grown CVD graphene and the transferred film has been recognised previously and is reported in the literature ^{158,159}. The reason behind this shift is mainly because the as-grown graphene is under strain ^{160,161} and doping ¹⁶². Following the reported literature values of I_{2D}/I_G and 2D FWHM that are characteristic of graphene morphology, it is relatively easy to determine the percentage coverage of graphene with a different number of atomic layers. Figure 4.3(d) shows that 98 % of the surface is covered with SLG and only 2 % has BLG coverage with no sign of FLG.

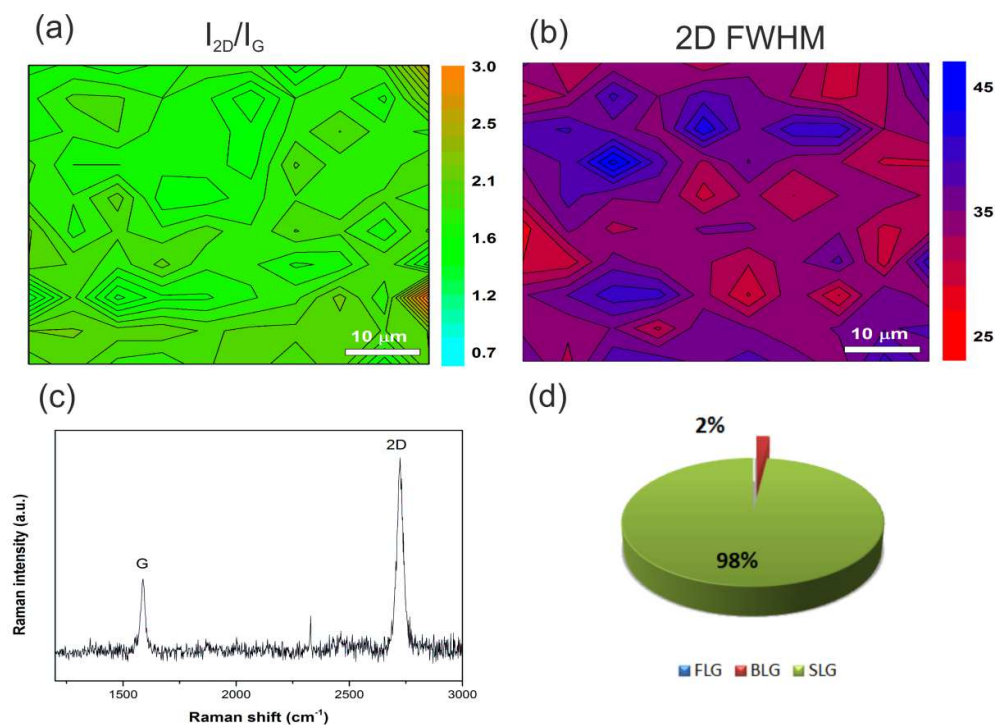


Figure 4. 3. Raman maps of CVD graphene grown at 1000 °C, 30 minutes growth time and a pressure of 0.1 mbar on 25 μm copper foil (a) I_{2D}/I_G (b) 2D band FWHM (c) Raman spectra of SLG. (d) The pie chart shows coverage statistics.

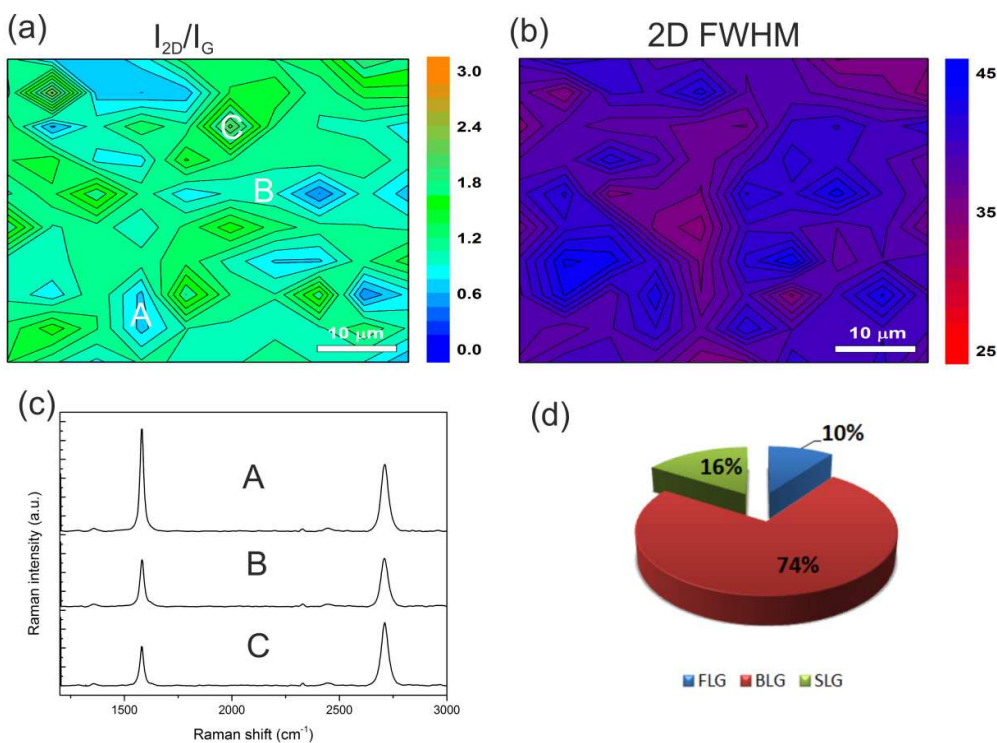


Figure 4. 4. Raman maps of CVD graphene grown at 1000 °C, 30 minutes growth time and a pressure of 0.1 mbar on 500 μm copper foil (a) I_{2D}/I_G (b) 2D band FWHM (c) Raman spectra: A FLG, B BLG, C SLG. (d) Pie chart shows coverage statistics.

When thicker Cu substrates (500 μm) are used under the same growth parameters, Raman spectroscopy mapping produces results that are different from those found with the thin (25 μm) copper foil. It is clear from Figure 4.4(a)-(b) that BLG dominates the coverage. Referring to the pie chart (Figure 4.4(d)), the thicker substrate surface is covered with 16 % SLG, 74 % BLG and 10 % FLG. Contributed with coverage with Raman spectra of the three different graphenes, labelled A, B and C on the I_{2D}/I_G map.

SEM micrographs (Figure 4.5) reveal the differences in topography between the two Cu substrates used in this study. Films were grown on the 25 μm thick copper foil show uniform contrast with almost full surface coverage and a few darker contrast points. While it is pronounced from the images that the film grown on the 500 μm thick Cu substrate (Figure 4.5(b)) show dark contrast and irregular grain shapes, furthermore, it is discontinuous.

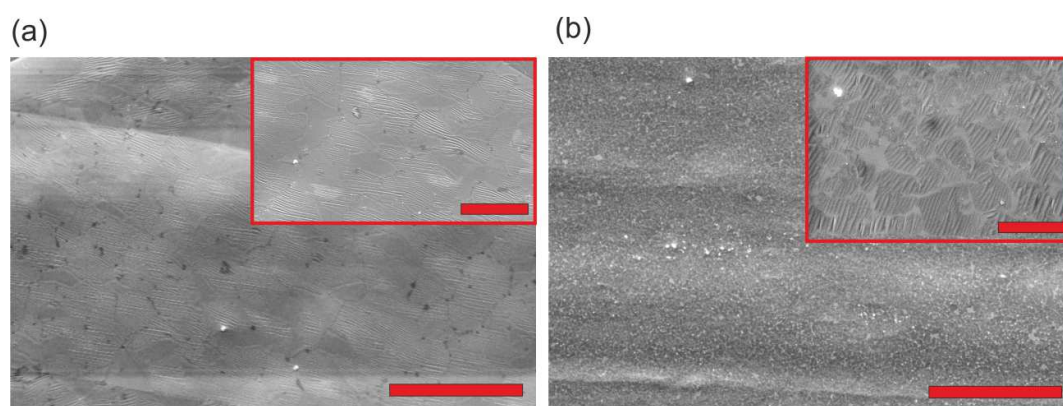


Figure 4. 5. SEM micrograph of graphene grown at 1000 $^{\circ}\text{C}$, 30 minutes growth time and a pressure of 0.1mbar on (a) 25 μm copper thick. Scale bar:20 μm . Insert higher magnification of the same area. Scale bar:10 μm . (b) 500 μm thick. Scale bar:20 μm . Insert higher magnification image. Scale bar:2 μm .

When growth time is increased from 30 minutes to 150 minutes, graphene grown on the thin Cu foil still shows uniformity and almost the same graphene quality as for 30 minutes growth time (Figure 4.6(a)-(c)). This is consistent with reports in the literature that SLG is not a catalyst for further hydrocarbon decomposition, therefore as soon as a

full SLG coverage graphene film is achieved, the copper surface loses its catalytic activity^{111,163}.

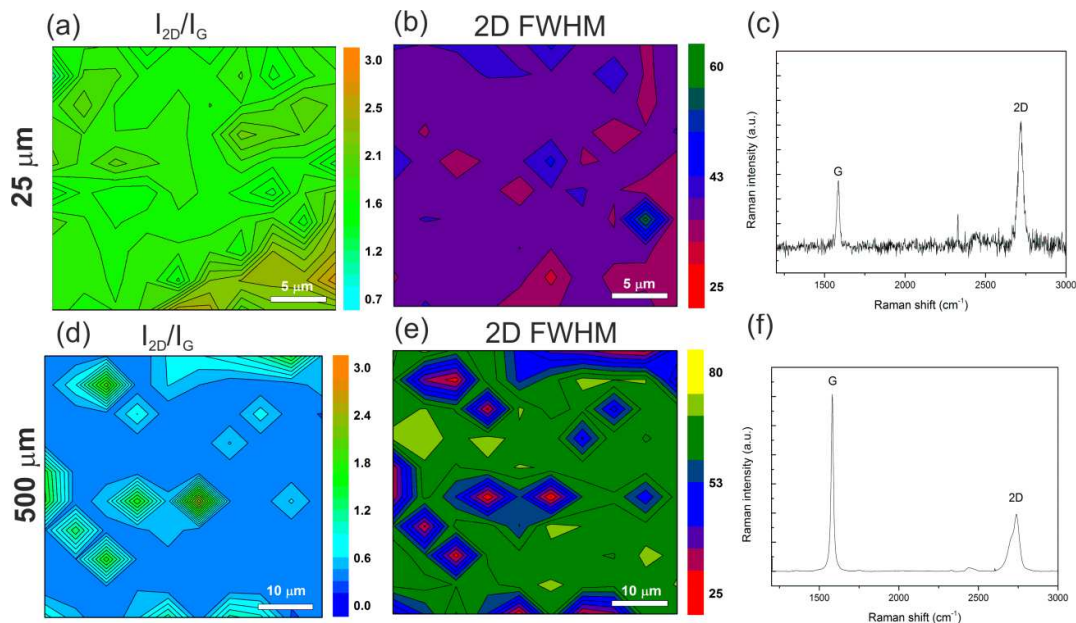


Figure 4. 6. Raman I_{2D}/I_G , 2D band FWHM maps and spectrum of CVD graphene grown at 1000 °C, 150 minutes growth time and a pressure of 0.1mbar on 500 μm copper foil (a)-(c) and 25 μm (d)-(f).

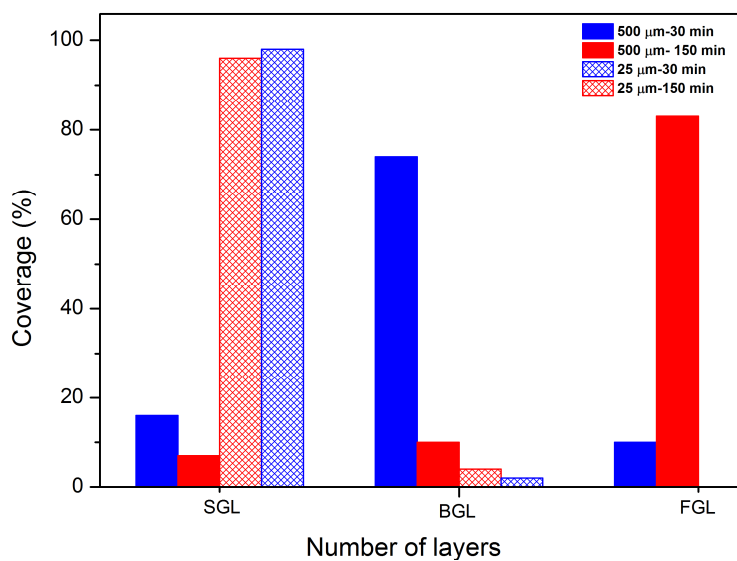


Figure 4. 7. Statistics bar graph shows a number of graphene layers vs coverage percentage for graphene grown on 25 μm and 500 μm at different growth periods (30 minutes and 150 minutes).

However, Raman maps of the films grown on thick Cu foil indicate FLG and even a few graphite points when the growth time is increased five times, Figure 4.6(d)-(f). The FWHM of the 2D band map shows that the range $\sim 60\text{-}70\text{ cm}^{-1}$ is dominant. Furthermore, $\sim 80\%$ of I_{2D}/I_G ratio is between $\sim 0.2\text{-}0.8$ with a few points ≥ 1.5 . To get a clear judgment of the behaviour on both substrates, graphene layers statistics from both thick and thin foils are presented in one bar chart (Figure 4.7). It is clear that the $25\text{ }\mu\text{m}$ thickness Cu foil shows almost no change when the exposure time is increased. However, $500\text{ }\mu\text{m}$ thick Cu substrate shows a significant change in the percentage of FLG coverage as exposure time is increased.

4.3.1. Impact of copper substrate thickness

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 the author's knowledge. This might be attributed to the fact that the influence of carbon solubility in copper is neglectable and that graphene growth is mainly attributed to the catalytic decomposition of the hydrocarbon on the copper surface¹¹¹. Another possible reason is the cost of thin foils compared with thick ones and, possibly, more importantly, the time required to etch a thin foil (when transferring graphene) is less than for a thick foil. This is supported by surveying the literature on CVD graphene film growth on copper substrates (Figure 4.8). This survey reveals that 83% of published literature used $25\text{ }\mu\text{m}$ thickness copper substrates with fewer reports of $50\text{-}125\text{ }\mu\text{m}$ substrates. However, Fange et al. studied the effect of copper substrate thickness on BLG formation on the outside surface of a copper enclosure. Their results confirmed that by reducing substrate thickness from $125\text{ }\mu\text{m}$ to $57\text{ }\mu\text{m}$, more carbon diffusion occurs from the inside to the outside surface, which leads to an increase in coverage of trilayer and quadlayer films¹⁶⁴.

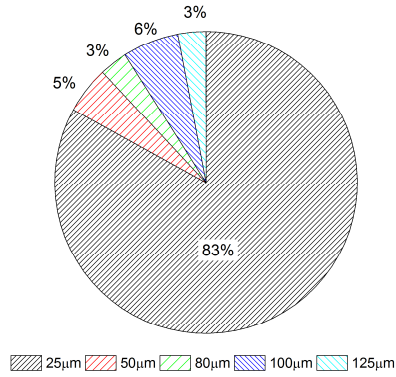


Figure 4. 8. Pie chart shows the percentage of copper substrate thickness used in CVD graphene growth as reported in the literature^{165–198}.

Further investigation of the effect of copper substrate thickness on the mechanism of CVD graphene growth required more study of different copper substrate thicknesses under the same growth conditions. Two further copper substrates were added to the study, ordered from the same supplier, with thickness values of 250 μm and 1000 μm as indicated in Table 4.1.

Table 4. 1. Copper foils used in CVD graphene growth study.

Thickness (μm)	Supplier	Purity	Product number	Pre-treatment
25	Goodfellow	99.9%	CU000359	As received
250	Goodfellow	99.99%	LS467111	As received
500	Goodfellow	99.99%	LS459922	As received
1000	Goodfellow	99.99%	LS445218	As received

Figure 4.9 shows Raman I_{2D}/I_G map, 2D FWHM map and SEM images for four different copper substrate thicknesses. Reading Raman maps and looking at SEM images, the variation in graphene coverage with copper thickness is clear. Further analyses of the data in Figure 4.9 are required to define the number of graphene layers on the surface.

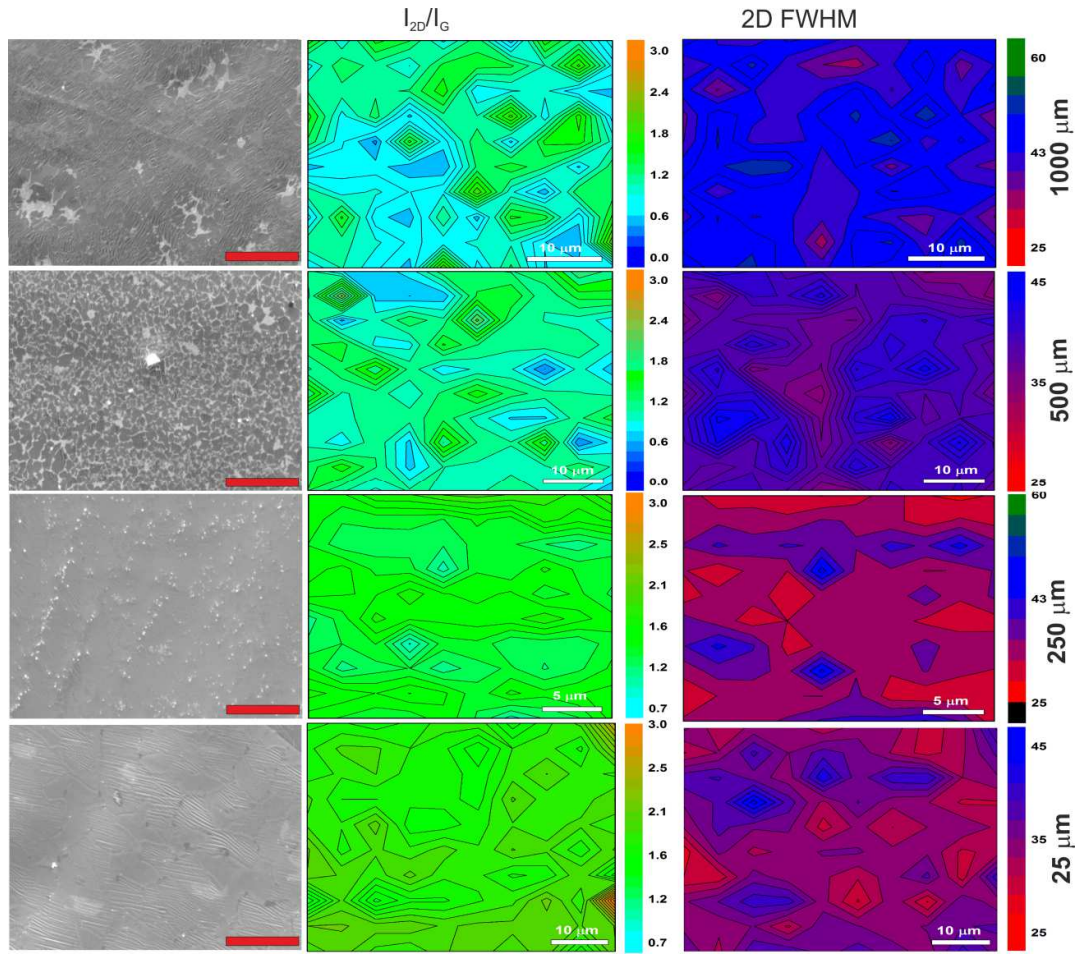


Figure 4. 9. Raman spectroscopy I_{2D}/I_G and 2D FWHM maps with SEM images (scale bar:10 μm) of catalytic CVD graphene grown at 1000 °C, 0.1 mbar and 30 minutes on 25 μm , 250 μm , 500 μm and 1000 μm copper thicknesses.

Figure 4.10 shows the percentage of SLG surface coverage of the graphene film with different layer thickness, based on the Raman spectroscopy map (Figure 4.9), plotted against substrate thickness. This shows the effect of substrate thickness on graphene number of layers. SLG coverage shows a decrease with increasing substrate thickness, declining from 98 %, for 25 μm thick copper foil, to 16 % for 500 μm and 1000 μm foils. However, both BLG and FLG coverage increases with increasing substrate thickness.

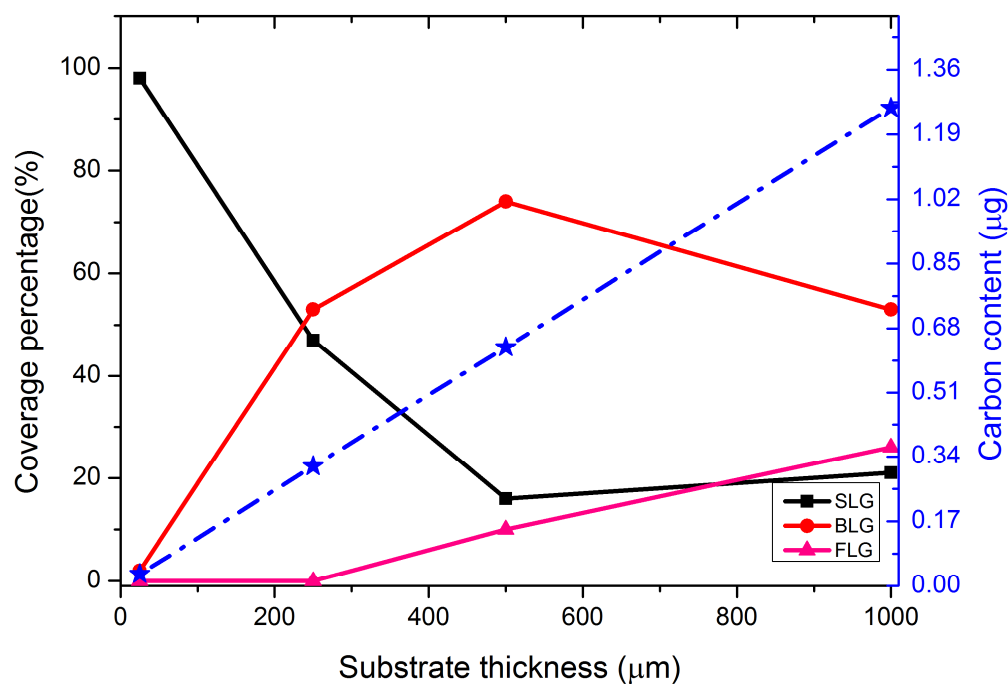


Figure 4. 10. Distribution graphene coverage vs copper substrate thickness. Blue dash line calculated carbon content for each copper thickness.

4.3.2. Possible growth mechanism

To interpret the increase of graphene layers number with increasing substrate thickness we inspect the Cu-C phase diagram (Figure 4.2(a)). At growth temperature (1000 °C) the equilibrium C content in Cu is low) and experimentally, the value reported by McLellan is 0.005 wt.%¹⁹⁹. Lopez et al. measured carbon solubility by an improved combustion analysis, which shows values 50 times smaller than reported data (1.4 ± 0.1 wt.ppm at 1010 °C)¹⁹⁹. From this, he modified the Cu-rich side in the Cu-C equilibrium phase diagram as depicted in Figure 4.11. Carbon solubility in copper might be very low and is usually neglected for small copper volumes (e.g. the 25 μm thick substrate), however, when the copper substrate thickness increases, its effect should be considered. Considering Figure 4.10, the amount of dissolved carbon increases with increasing copper volume. For example, a 1 cm × 1cm area of the 25 μm thick copper substrate can dissolve 0.03136 μg of carbon at 1000 °C (taking the carbon solubility value as 1.4

wt.ppm). However, the same area of the 1000 μm substrate can dissolve about 1.2544 μg under the same conditions. To fully cover 1 cm^2 of copper substrate by SLG requires 3.81×10^{15} carbon atoms, which is about 0.08 μg of carbon. This value can be used to estimate how many layers of graphene can form from the dissolved carbon in the copper volume. For the 25 μm substrate, the dissolved carbon in bulk can form 0.4 SLG that is

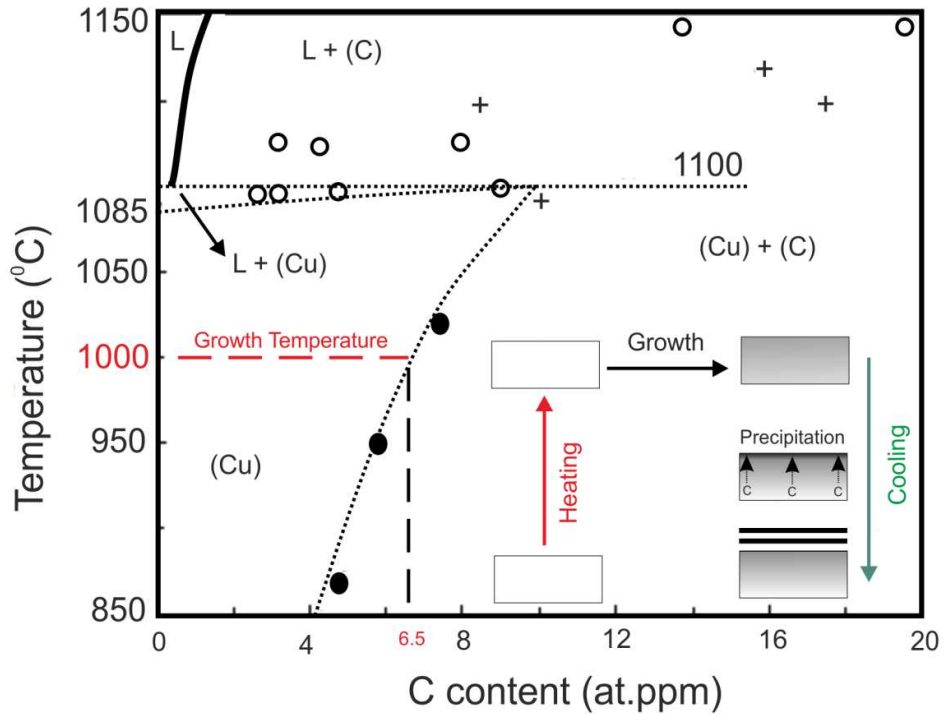


Figure 4. 11. Equilibrium phase diagram of the Cu-C system at the Cu rich side¹⁹⁹ with the schematic diagram of proposed graphene growth cycle on Cu. During annealing process, carbon concentration inside Cu bulk assumed zero. Carbon liberated at 1000 °C by thermal-catalytic decomposition process and its dissolve value related to Cu thickness.

less than the amount required for complete SLG coverage. Therefore, this might suggest that the majority of the graphene film forms through surface reaction growth, which agrees with our experimental results and literature values¹¹¹. However, the amount of carbon dissolved in the 1000 μm thick substrate is sufficient to grow 16.47 SLG layers, assuming the carbon segregates to the surface during cooling. The proposed film growth

cycle is shown schematically in Figure 4.11 in conjunction with the part of the Cu-C phase diagram of most interest for our experimental conditions. During heating and annealing under hydrogen, the copper substrate is assumed to have zero carbon content. When methane gas is passed through the CVD reactor at 1000 °C, carbon starts to be liberated by catalytic-thermal decomposition at the surface and diffuses into the metal bulk. Given sufficient time, the carbon will fully saturate the metal. When the precursor gas flow is stopped, and the sample starts cooling down to room temperature, the carbon solubility value decreases, and carbon diffuses towards the metal surface. Therefore, the influence of carbon solubility increases when the substrate volume increases and in turn the amount of carbon that diffuses from bulk-to-surface increases as well until the saturation limit is achieved.

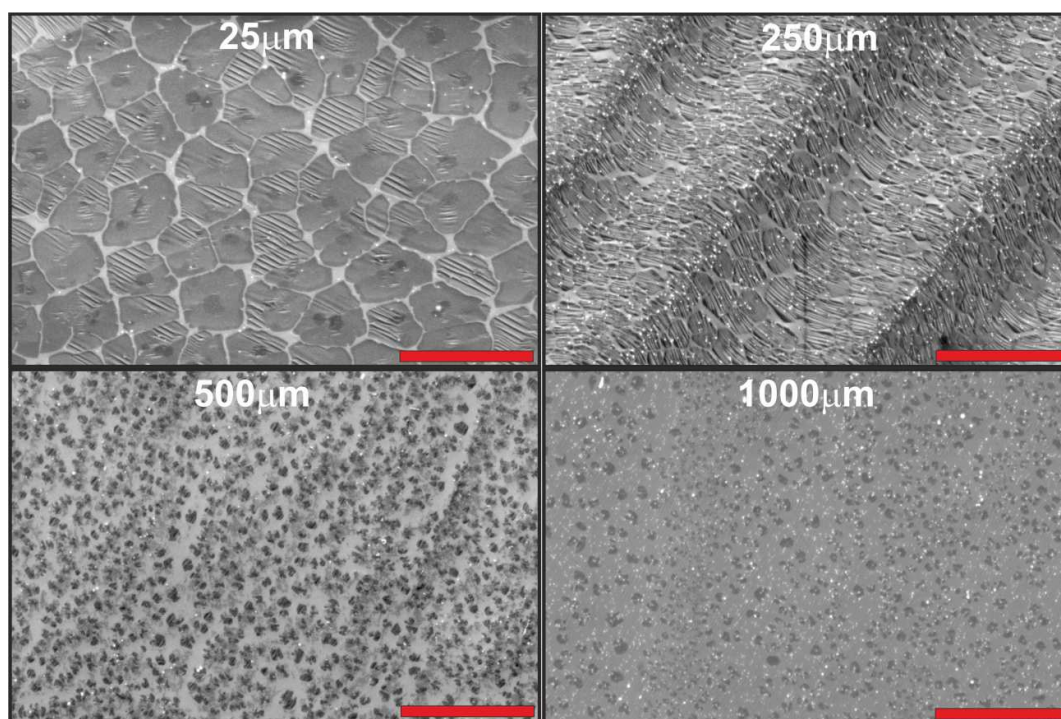


Figure 4. 12. SEM images of graphene grown on 25μm, 250μm, 500μm and 1000μm thickness copper substrates at 1000 °C, 0.1 mbar, 2:1 CH₄: H₂ and 40second growth time. Scale bar: 10μm.

Based on this hypothesis copper substrates with smaller thickness will saturate quicker than those of high thickness. To test this, growth times were reduced as much as possible and growth performed under the same process conditions (pressure, temperature and CH₄: H₂ ratio) on the same substrates. With a short growth, time (40 seconds), copper substrate thicknesses of 25 μm , 250 μm , 500 μm , and 1000 μm shows different film grain size and coverage. From SEM micrographs, the estimated grain size is $\sim 4 \mu\text{m}$, 1.8 μm , 0.85 μm , and 0.75 μm for the 25 μm , 250 μm , and 500 μm and 1000 μm substrate thickness respectively. Furthermore, surface coverage also changed with substrate thickness, *i.e.* larger surface coverage ($\sim 80 \%$) was observed for thin substrates, while a smaller area coverage was recorded for thick substrates (Figure 4.12).

4.3.3. Growth at different temperature and pressure

It is clear that the use of different thickness copper substrates has a significant influence on the morphology of the CVD grown films. If our proposed mechanism of the diffusion of C into the substrate, followed by rejection of carbon on cooling, is correct we would expect the substrate temperature and gas pressure to both influence the morphology of the grown films.

CVD experiments were carried out using the same CH₄: H₂ ratio by volume (2:1) and growth time (30 minutes), with the growth performed over a range of temperatures (600 - 1000 °C) and with background pressure between 0.1 and 0.65 mbar. For low pressures of 0.1 mbar, at 600 °C the Raman spectra of the films only show a G peak at position $\sim 1594 \text{ cm}^{-1}$ and a D peak at $\sim 1361 \text{ cm}^{-1}$ with no sign of a 2D peak (Figure 4.13). This Raman feature is believed to be a fingerprint of amorphous carbon²⁰⁰. Interestingly, the intensity of the G band and D band both decreased at 700 °C and had completely

vanished at 800 °C. This is probably because the carbon desorption rate at this growth temperature is larger than the adsorption rate due to the evaporation of copper from the surface²⁰¹. SEM images (Figure 4.13) shows that surface roughening begins at 700 °C with obvious steps forming at 800 °C. Increasing the growth temperature to 900 °C and 1000 °C, graphene starts to grow which is indicated by the G and 2D Raman bands in conjugation with the SEM images. The increase of the growth pressure to 0.65 mbar, at 600 °C and 700 °C growth temperature leads to the growth of amorphous C, however, at 800 - 1000 °C we observe a 2D peak, which indicates graphene growth on the surface (Figure 4.13).

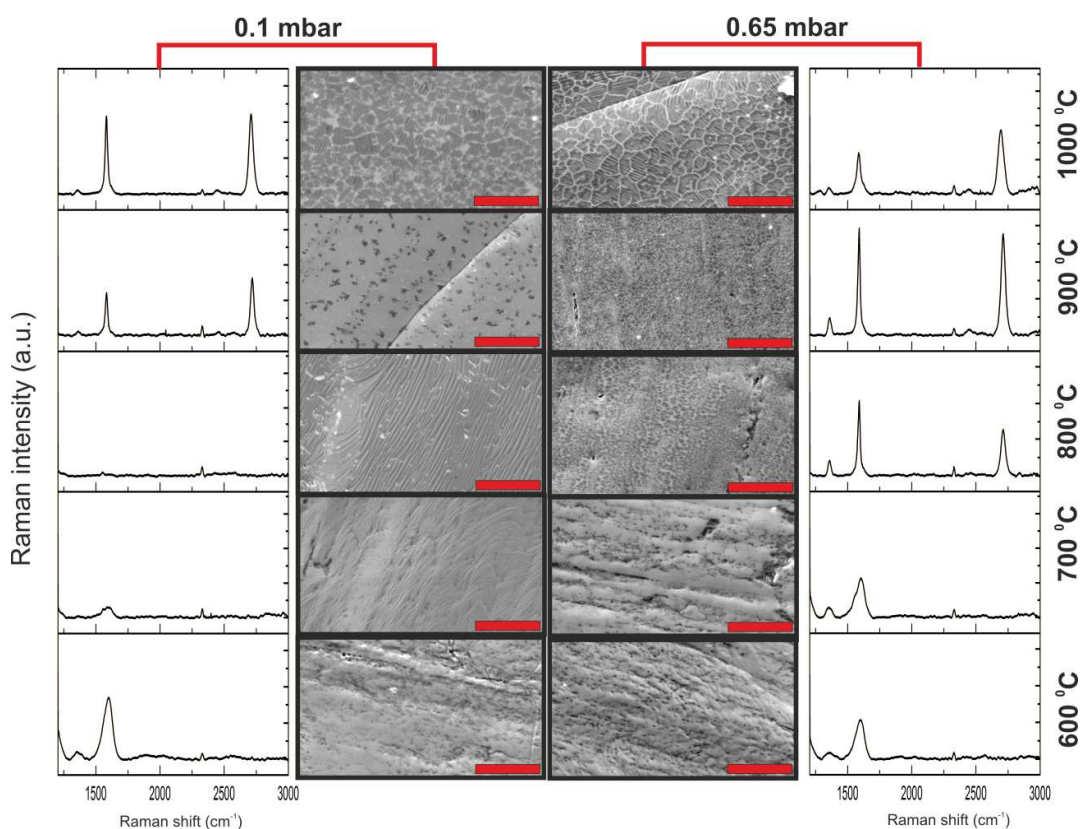


Figure 4. 13. Panel shows Raman spectrum and correspondence SEM micrograph for CVD graphene grown over a 500μm copper substrate. The growth conditions are as follows: temperatures 600 -1000 °C, pressure 0.1 and 0.6 mbar, CH₄: H₂ ratio 2:1 and exposure time 30 minutes. Scale bar: 5μm.

Since growth pressure in the CVD system is controlled by flow rate, *i.e.* increasing total gas flow rate increase the chamber pressure, therefore, increasing growth pressure, is accompanied by an increasing carbon concentration in the reactor. At 800 °C growth temperature and 0.1 mbar background pressure, no graphene growth occurs because the carbon desorption rate is higher than the adsorption rate. However, when the pressure is increased to 0.65 mbar, the concentration of carbon increases as well and therefore the adsorption rate is higher than desorption rate²⁰¹.

4.4. CVD growth of graphene on Nickel

Repeating the same growth conditions with 500 µm thick Ni substrate shows a thicker graphitic film forming on the surface. Raman spectroscopy and SEM images confirm the growth of a graphite layer (Figure 4.14). The carbon solubility in Ni is much greater than in Cu, and this difference influences the film growth times. We have noticed that no growth occurs on the Ni surface before 210 mins, which is different from Cu substrates which require very short growth times of < 1min.

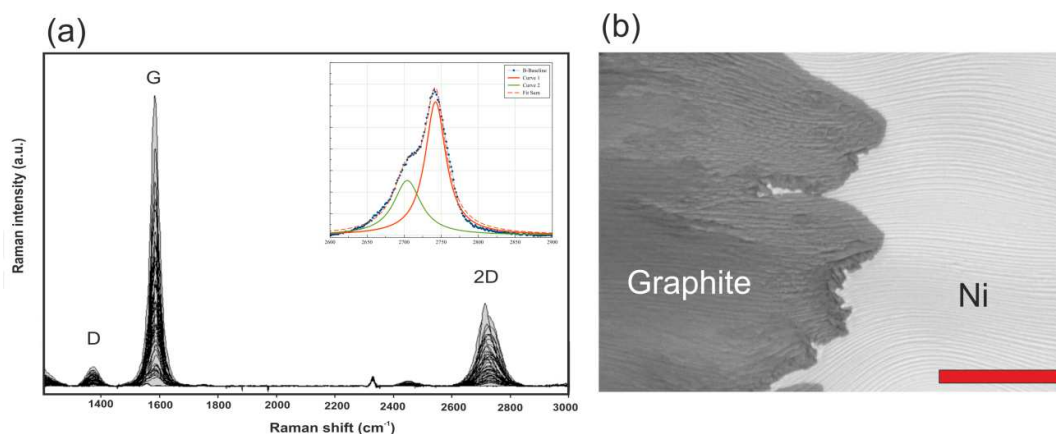


Figure 4. 14. CVD graphene on 500 µm Nickel substrate at 1000 °C, 0.1 mbar, CH₄: H₂ 2:1 and 210 minutes growth time. (a) a 100 point Raman spectrum (insert: 2D band fitting). (b) SEM image. Scale bar: 5 µm.

Weatherup et al. defined this period before the growth of a graphitic film on the catalytic surface as the “incubation period”²⁰². This is the time required to saturate the substrate with carbon before any nucleation process can take place. The incubation period is related to the ability of the Ni substrate to dissolve a specific amount of carbon, which in turn is highly dependent on the substrate thickness. Therefore, growth performed under the same conditions with different thicknesses of Ni shows a linear relationship between a substrate thickness and the time needed to achieve a surface saturated with carbon (Figure 4.15). The mechanism for CVD graphene growth on Ni is a diffusion-segregation process, *i.e.* the Ni bulk acts as a carbon reservoir that, during the cooling process, segregates carbon to the surface, therefore controlling the amount of carbon that segregates from the bulk to the surface has great impact on the produced graphitic film.

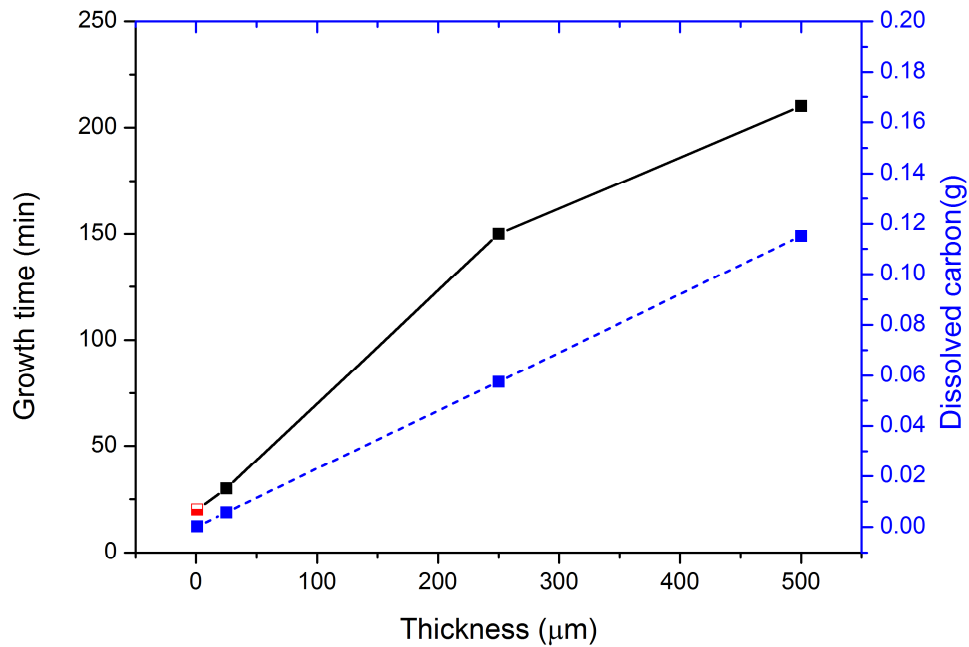


Figure 4. 15. CVD of graphene on three different Ni foil thickness, 25μm, 250μm and 500 μm. The red marker is 1μm Ni /SiO₂/Si film substrate. Blue dash line calculated carbon content for each nickel thickness. Growth conditions, 1000 °C, 0.1 mbar, CH₄: H₂ 2:1.

One of the strategies used to control the Ni bulk reservoir effect is to reduce the reservoir volume itself, *i.e.* grow on a low thickness substrate. Growing on reduced Ni thicknesses (250 μm and 25 μm) shortens the incubation and hence the growth time, however, the graphitic film quality is the same due to high carbon amount that is dissolved and precipitates on the substrate surface (Figure 4.15). The dissolved carbon in Ni can be reduced by reducing Ni thickness, therefore, by using thin film technology 1 μm thick Ni films were deposited by magnetron sputtering on SiO₂/Si surfaces. One of the advantages of using thin films is the ability to form a flat Ni surface, which does not need any further surface preparation processes⁸⁸. Moreover, using thin catalytic films is a good technique to control the number of segregated graphene layers²⁰³. Raman mapping results from CVD graphene grown on 1 μm Ni/SiO₂/Si film is presented in Figure 4.16. It is clear from the collected Raman I_{2D}/I_G ratio that the distribution of the number of graphene layers is improved compared with the massive Ni foil (Figure 4.14) which was almost completely covered with graphite. From the I_{2D}/I_G map, the coverage is estimated to be 70% FLG, 20% BLG, and 10% SLG. The non-uniform surface distribution of SLG, BLG and FLG is attributed to the polycrystalline nature of the film because the graphene flakes strongly depend on the underlying Ni grain size²⁰⁴. It is evident from SEM micrographs in Figure 4.16 (d)-(e) that the Ni film grain boundary density is high (grain size range 5.6-39.5 μm^2), which in turn can serve as nucleation sites for FLG and a pathway for carbon diffusion toward the bulk^{86,145}. The grain size of the Ni thin film deposited by sputtering depends on preparation conditions (substrate, substrate temperature, and pressure). Furthermore, annealing at high temperature ~ 1100 °C under hydrogen might increase the grain size⁸⁸.

Segregation of carbon to the Ni surface has been studied intensively by Blakely and co-workers^{74,112,205}.

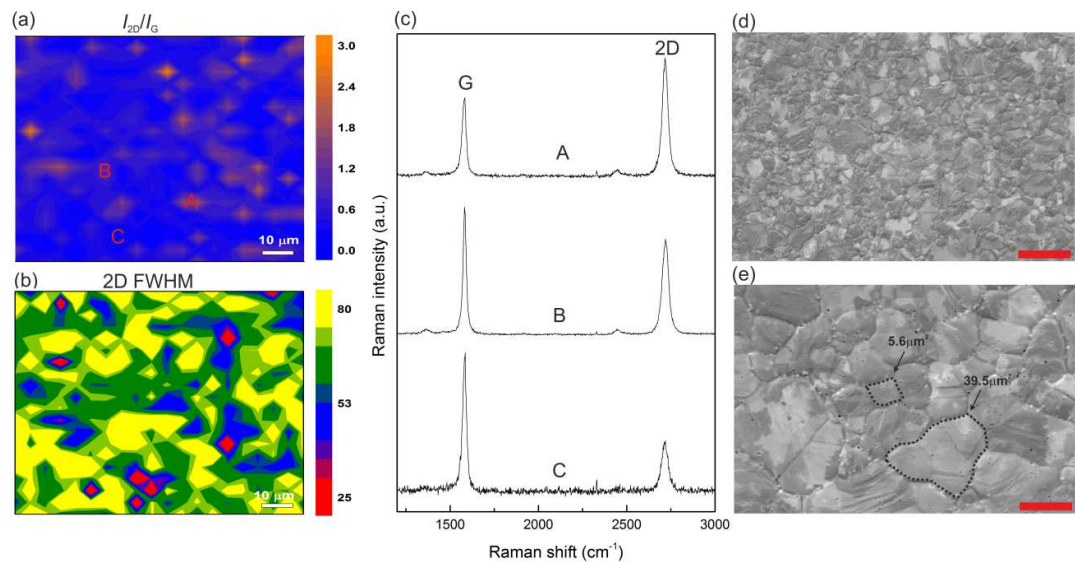


Figure 4. 16. CVD of graphene on 1 μm Ni/SiO₂/Si film substrate. (a) moreover, (b) I_{2D}/I_G and 2D FWHM Raman maps respectively. (c) Raman spectrum labelled in the map. (d) and (e) SEM images of graphene/Ni thin film. Scale bar: 20 μm and 5 μm respectively. Growth conditions, 1000 °C, 0.1 mbar, CH₄: H₂ 2:1 and 30 minutes growth time.

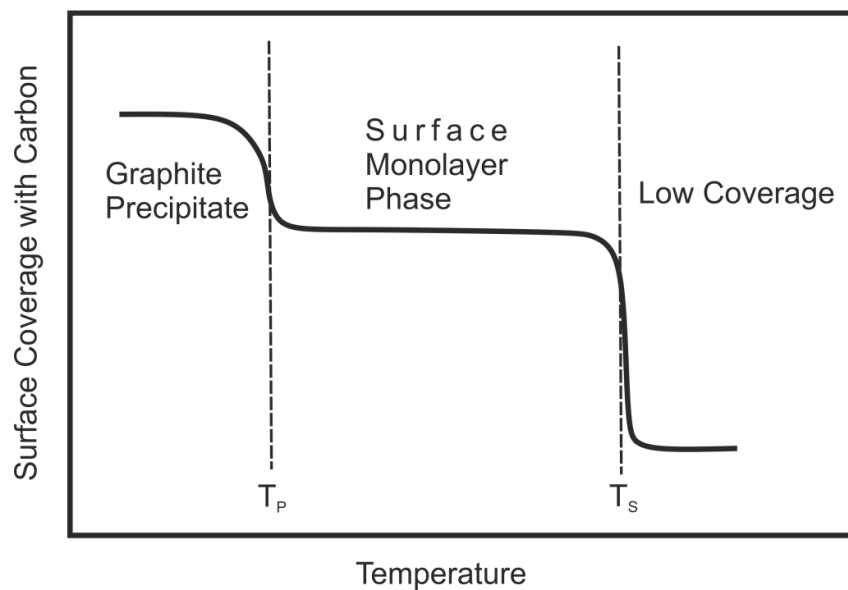


Figure 4. 17. Schematic diagram shows the dependence of the three Nickel surface coverage states on temperature. Graphene segregates at T_S (segregation temperature) and graphite precipitate at T_P (precipitation temperature) point ⁷⁴.

Their work identified three different states; low carbon coverage, which is comparable to the concentration of carbon in bulk, this usually happens at high temperature. Carbon monolayer coverage, which forms at the intermediate temperature, the stability of this phase is over ~ 100 C° (between 1100 C° and 1000 C°). The third phase is graphite precipitation that covers the surface at low temperature (Figure 4.17). Blakely attributed graphene formation on the Ni surface at high temperature to the greater binding energy or entropy/carbon atom in the graphene⁷⁴.

Ramanathan and Blakely evaluated the equilibrium concentration of adsorbed carbon atoms from a CH₄/H₂ gas mixture on Ni (111) surface²⁰⁶. Their calculation is based on Dunn, McLellan and Oates solubility data and Eizenberg and Blakely equilibrium segregation data⁷⁴. In a system containing a CH₄/H₂ gas mixture in equilibrium with Ni, carbon may exist in three locations: in the gas phase, on the Ni surface and in the Ni bulk. Assuming the carbon in all these states is in equilibrium, the carbon solubility limit and segregation limit in terms of gases partial pressure can be expressed respectively²⁰⁶:

$$\ln(p_{CH_4}/p_{H_2}^2) = -13.36 + 0.95/kT_P \quad 4.1$$

$$\ln(p_{CH_4}/p_{H_2}^2) = -13.72 + 0.89/kT_S \quad 4.2$$

Figure 4.18 is a plot of equation (4.1) and (4.2) versus the reciprocal of temperature.

The diagram is divided into three zones:

1. Three-dimensional graphite precipitates,
2. Dilute surface coverage
3. A condensed monolayer phase in between (1) and (2).

To get more advantage from the diagram, experimental values collected from the literature are plotted on the diagram. Scattered experimental points reveal that working

in graphite precipitate zone is more likely, including even this work (the red marker). This might be attributed to the fact that using a low $p_{CH_4}/p_{H_2}^2$ ratio needs, in principle, long growth times that eventually allow the bulk to become fully saturated with carbon, which segregates upon cooling²⁰².

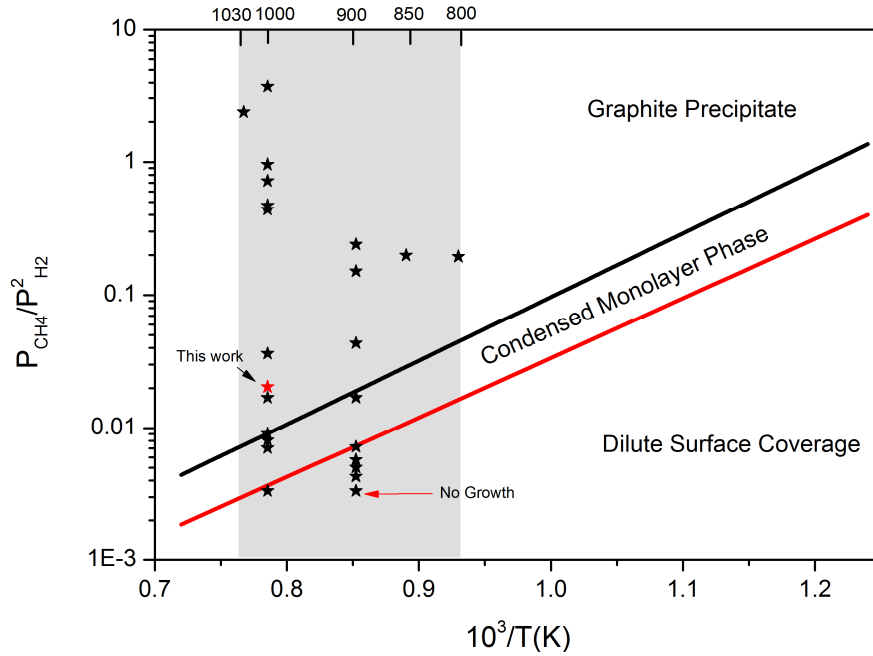


Figure 4. 18. Experimental solubility²⁰⁷ and segregation curve⁷⁴ of carbon in Ni with respect to CH_4/H_2 partial pressure at a different temperature. Scatter markers are experimental CVD data collected from literature^{86,145,203,208–214}. Red marker belongs to this work.

Working in the dilute surface coverage zone in conjunction with low growth temperature (900 °C) has also been reported by some groups⁸⁶. The benefit of reducing growth temperature is to lower carbon solubility (carbon solubility is 0.25 and 0.19 wt.% at 1000 °C and 900 °C H_2 respectively). Experiments in very dilute hydrocarbon atmospheres (6 sccm CH_4 /1400 sccm H_2 with $p_{CH_4}/p_{H_2}^2 \sim 0.004$) show no film growth (Figure 4.18), which is attributed to insufficient carbon released during the exposure period to hydrocarbon.

4.4.1. Impact of cooling rate

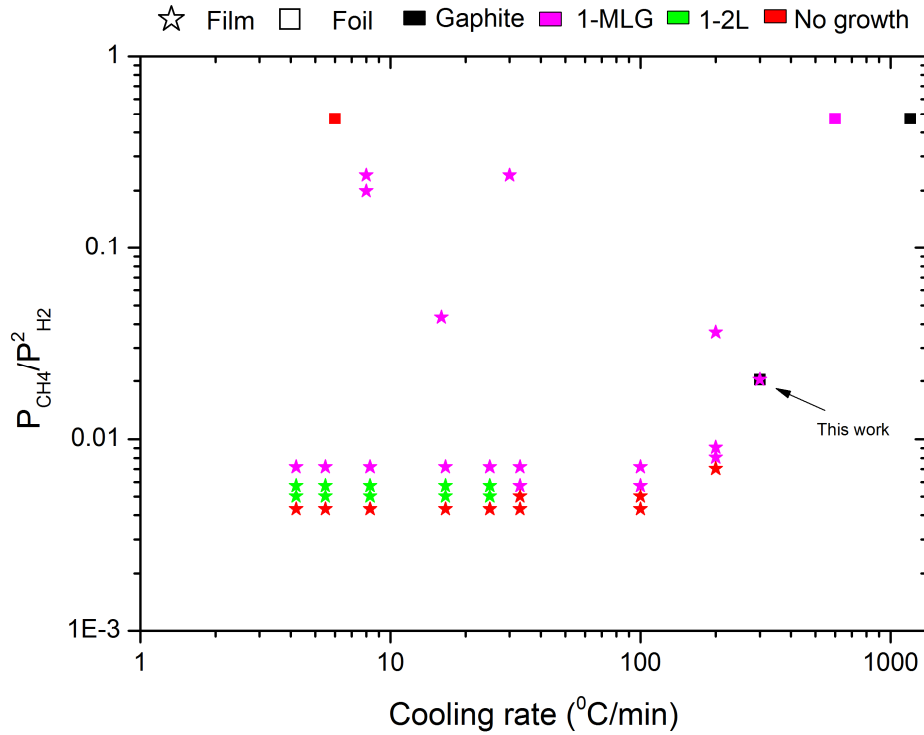


Figure 4. 19. Experimental data collected from literatures^{86,145,203,208–214} scattered on cooling rate vs CH_4/H_2 partial pressure.

Controlling the cooling rate of the Ni substrate during graphene growth has a significant impact on controlling the segregation process^{86,214}. Figure 4.19 shows the effect of cooling rate and hydrocarbon concentration on the resulting graphene film uniformity. At low methane concentrations ($p_{CH_4}/p_{H_2}^2 \sim 0.004$), the solute concentration to be segregated upon cooling is not sufficient to promote graphene formation on the Ni surface. However, increasing methane concentration ($p_{CH_4}/p_{H_2}^2$ 0.005-0.0055) results in the formation of 1-2LG, if the samples are cooled under low cooling rates, which helps to segregate carbon under equilibrium conditions⁸⁶. Further increase of methane concentration results in FLG at low and high cooling rates (Figure 4.19). The effect of Ni thickness is also clear, for this work, 1 μm and 500 μm Ni substrates were subjected

to the same growth conditions; in this case, the 1 μm Ni film promoted 1-ML graphene, while the 500 μm Ni foil gave graphite.

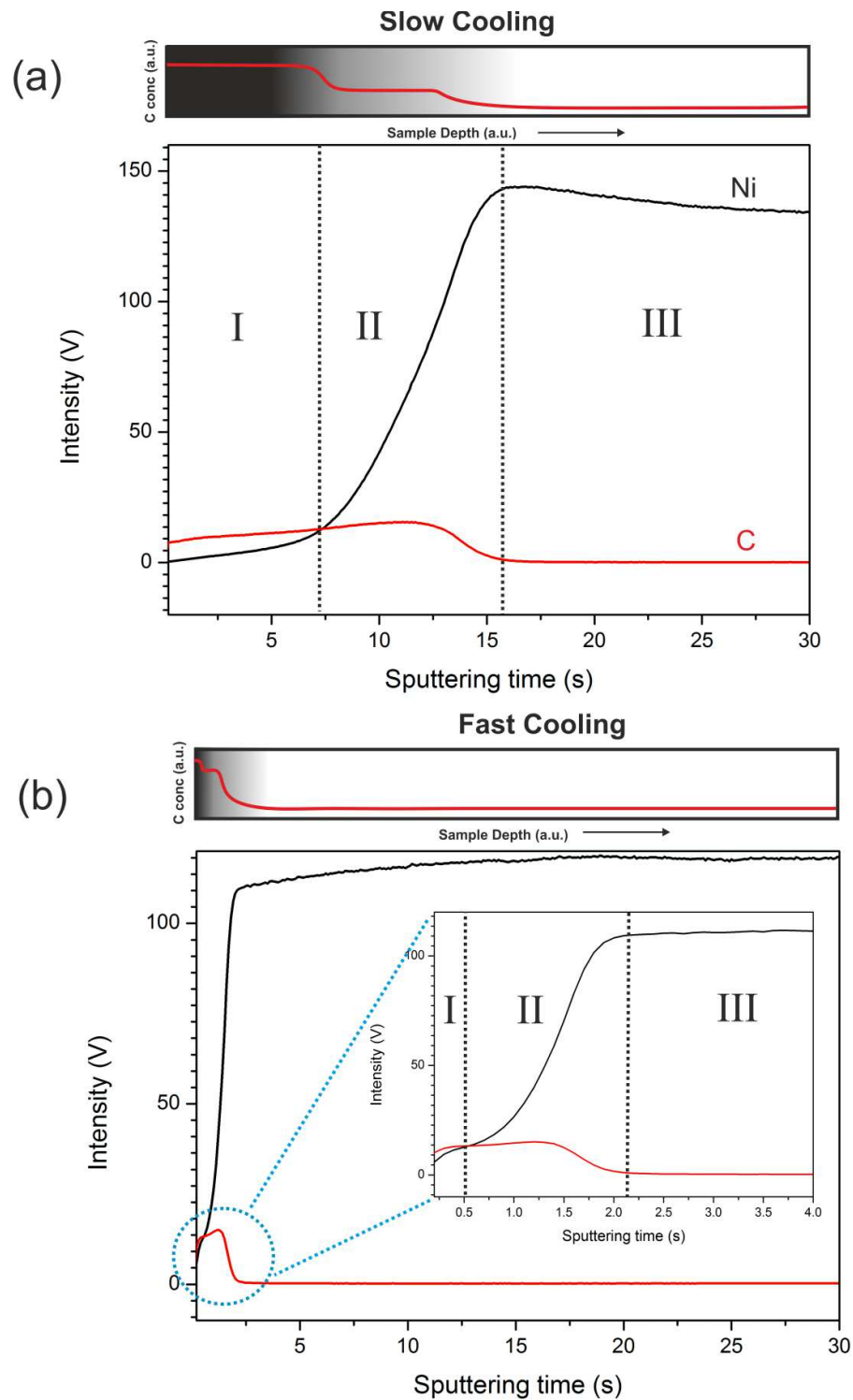


Figure 4. 20. GDOES Ni and C depth profile for CVD graphene grown at 1000 °C, 0.1 mbar and CH_4 : H_2 2:1. Cooling rates slow (27 °C/min) and fast (376 °C/min). Three identified regions, I (surface), II (subsurface) and III (bulk). Top 2-dimensional schematic diagram shows C diffusion in Ni with accordance to GDOES result.

To explore the effect of cooling rate in more detail, two Ni foils (500 μm) were exposed to the same growth conditions ($p_{\text{CH}_4}/p_{\text{H}_2}^2 = 0.0204$ at 1000 $^{\circ}\text{C}$) but cooled down at slow (27 $^{\circ}\text{C}/\text{min}$) and fast (376 $^{\circ}\text{C}/\text{min}$) cooling rates. Both samples were analysed with GDOES technique to see the difference in depth profile for the elements of interest (Ni and C). Figure 4.20 shows the difference between slow and fast cooling rates. The surface to the bulk region was scanned using a 30 second sputtering time. Interestingly, the depth profile shows three regions: region I represent the surface, II the subsurface and III the bulk. Cooling the substrate slowly from 1000 $^{\circ}\text{C}$ down to room temperature encourage more carbon atoms to diffuse toward the surface, which is clear from the depth (thickness of the graphitic film) of the region I compared with fast cooling. Region II is characterized by the Ni intensity increasing gradually until it reaches a constant value, which is the bulk. Moreover, the subsurface region is a Ni-C solid solution rich in carbon, which feeds the graphitic film on the surface during the cooling stage²¹⁵. At fast cooling rates, the subsurface thickness is five times smaller than at slow cooling, which in turn explains the variation in graphitic film thickness on the surface.

4.4.2. Effect of growth pressure

In CVD, the partial pressure of the precursor gas has a considerable influence on the resulting products^{216–218}. The effect of methane partial pressure on growth time has been investigated. The growth pressure is controlled by the total gas flow rate, by maintaining the $\text{CH}_4:\text{H}_2$ ratio fixed. The growth time shows a nonlinear behaviour with growth pressure, Figure 4.21.

Based on the Knudsen equation (equation 4.3) increasing gas pressure significantly increases the number of gas flux molecules²¹⁸.

$$J = 3.51 \times 10^{22} \frac{P}{\sqrt{MT}} \quad 4.3$$

Where J is flux in molecules/cm².sec., P is gas pressure in Torr, M is the gas molecular weight in g /mole, and T is the reactor temperature in Kelvin. However, not all molecules that strike the substrate take part in the growth process, because they need to stick (adsorb) on the surface first,



Therefore, calculating the adsorption-isotherm for each growth pressure will highlight the time-pressure trend. According to the Langmuir adsorption-isotherm model for a single adsorbate case, methane surface coverage (θ) can be calculated from the equation:

$$\theta_{CH_4} = \frac{K_{equ}P_{CH_4}}{1 + K_{equ}P_{CH_4}} \quad 4.5$$

Where P_{CH_4} is methane partial pressure in Pascals, K is the chemical reaction equilibrium constant, expressed by:

$$K = \frac{k_{forward}}{k_{reverse}} \quad 4.6$$

Moreover, k is the chemical reaction rate for the forward and reverse direction:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad 4.7$$

A is the pre-exponential factor, for forward reaction (adsorption) $A = 10$ (1/pa.s) and for reverse reaction (desorption) $A = 10^{13}$ (1/s), calculated according to Transition-State Theory²¹⁸. E is the activation energy barrier, for methane adoption on Ni is 0 (J/mole), and for desorption is 37550 (J/mole)²¹⁹. R gas constant (J/K.mol) and T is the temperature in Kelvin.

The results of the methane adsorption coverage calculation are presented in Figure 4.21. It is obvious from Figure 4.21 that methane coverage increases exponentially with increasing partial pressure. In fact, surface carbon concentration related directly to the number of methane molecules stick on the metal surface (surface coverage).

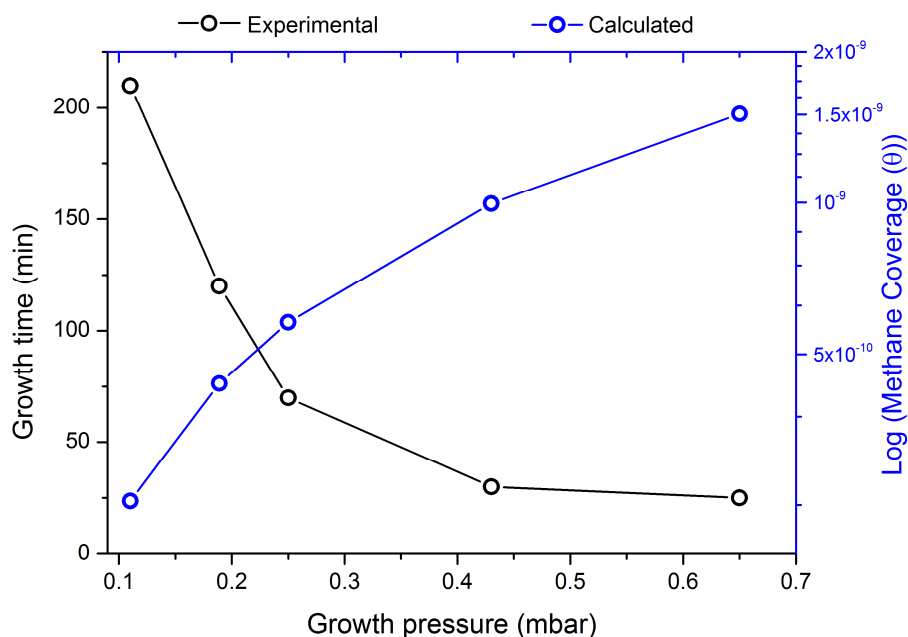


Figure 4. 21. Effect of growth pressure on CVD graphene growth time. Blue solid line is a calculated methane coverage θ .

Consequently, high carbon surface concentration encourages short growth times, *i.e.* 210 minutes at pressure 0.11 mbar reduces to 25 minutes using 0.65 mbar pressure.

4.5. Conclusion

In conclusion, chemical vapour deposition of graphene on two pure metals (Cu and Ni) having the same thickness has been performed and the resulting films characterised. CVD graphene on 500 μ m Cu leads to ~ 74% BLG comparing with 96% SLG on 25 μ m under the same growth conditions. The effect of Cu thickness on film composition is significant as revealed by Raman spectroscopy data from four different Cu thicknesses. SLG coverage declines with increasing Cu thickness while both BLG and FLG

coverage increases. We attribute this behaviour to the quantity of dissolved carbon that increases with increasing Cu thickness. On the other hand, CVD of graphene on Ni needs longer growth times (up to 210 minutes), which is required to achieve the surface or subsurface saturation condition. Raman fingerprints of the films on Ni substrates confirm they are graphite. The mechanism of graphene growth by CVD on Ni is diffusion–segregation, where substrate thickness, carbon solubility and cooling rate all have an impact on the grown film. GDOES depth profiles of Ni and C from the sample cooled at low and fast rates identified three zones. The surface which is almost a graphite film; subsurface, which is a C rich C-Ni solid solution, and the bulk which is a Ni rich C-Ni solid solution. The subsurface zone expands during slow cooling and shrinks with fast cooling, which in turn influences the segregated graphite layer on the surface.

5. CVD of graphene on Cu-Ni alloys

5.1. Introduction

Copper and nickel are adjacent elements in the periodic table; moreover, their atomic numbers (29 for Cu and 28 for Ni) and atomic weights (63.54 for Cu and 68.71 for Ni) are very close. They are also completely mutually soluble in both the liquid and solid state as shown in their equilibrium phase diagram²²⁰, Figure 5.1.

Nickel is commonly used as a catalyst in the steam reforming reaction to convert natural gas, such as methane, to hydrogen and carbon dioxide. However, poisoning of the catalyst occurs by the deposition of elemental C which is a challenging problem for its use^{221–225}. Catalyst surface deactivation by C deposition has been intensively studied in the past and one method found useful to increase the catalyst lifetime by alloying it with a less active metal for hydrocarbon decomposition, such Cu²²⁶.

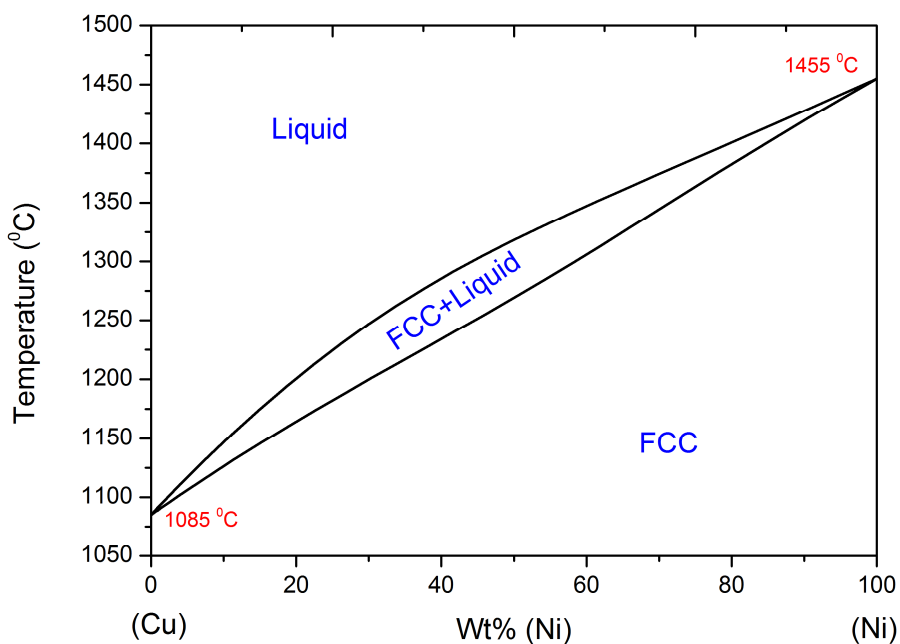


Figure 5. 1. Cu-Ni phase diagram. Adopted from²²⁰.

The catalytic activity of Cu -Ni alloys for hydrogenation reactions has been investigated intensively ^{226–230}. Dowden and Reynold found that Ni activity toward benzene conversion declines rapidly after adding Cu to the alloy and they attributed this to Cu valence electrons filling the Ni 3d-band holes (Figure 5.2(b)) ²³¹.

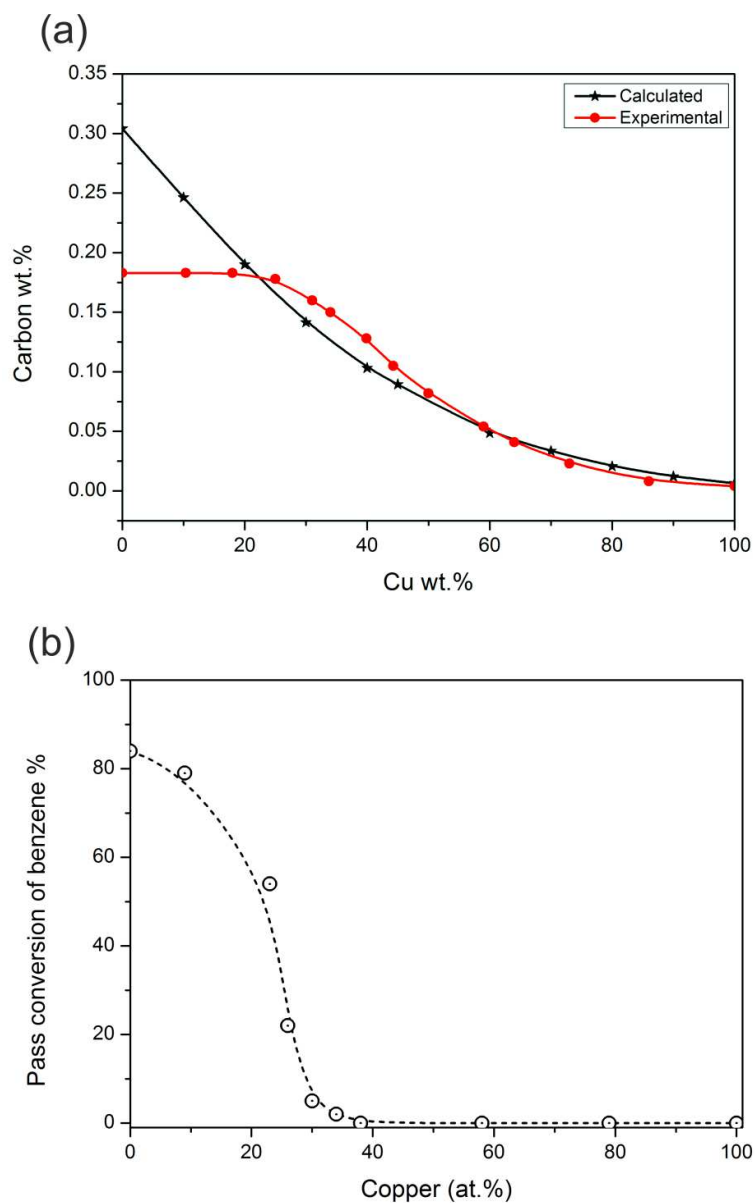


Figure 5. 2. (a) C solubility in Cu-Ni alloy as measured experimentally ²³² and calculated by Pandat ¹⁵⁷. (b) Effect of Cu content on Ni activity in benzene hydrogenation at 1 atm and 100 °C ²³¹.

Both theoretical studies and experimental results have found that alloying Ni with Cu decreases C solubility in the Cu-Ni system (Figure 5.2 (a)). Combining the high

catalytic activity of Ni with the low C solubility of Cu is a promising route to control a number of layers of graphene during film growth. Xie et al. reported the growth of 300 μm domain size AB-stacked BLG with the Cu vapour assistance on 25 μm thick electrodeposited Cu85-Ni15 alloy²³³. Liu and co-workers achieved 95% SLG graphene coverage on a 300 nm Cu94.5-Ni5.5 film substrate, however, by increasing the Ni content to 10.4 % the produced graphene was 89% BLG²³⁴. Ruoff et al. have investigated the CVD of graphene on commercial Cu31-Ni67.8²³⁵ and Cu90-Ni10²³⁶ alloy; they found that the thickness of precipitated graphene is influenced by both growth temperature and cooling rate. Cu-Ni alloy thin film have been previously used to synthesize graphene, Jeon et al. found that the number of graphene layers can be controlled by controlling the Ni content in the Cu-Ni thin film²³⁷. Prior studies using Cu-Ni alloys as a catalytic substrate for CVD graphene are limited both in number and composition range studied²³⁴⁻²⁴⁴, therefore further study is required. In addition to studying the feasibility of CVD growth of graphene on Cu-Ni alloy substrates, this work will also provide a better understanding of the role of C solubility in catalytic solid substrates.

This chapter presents results from experiments on the CVD growth of graphene on Cu-Ni alloys with composition Cu weight percent 70, 55 and 33 with the balance weight of Ni. These experiments are compared to films grown under similar conditions on pure Cu and Ni substrates.

5.2. Results

5.2.1. Raman spectroscopy

Figure 5.3 shows the I_{2D}/I_G and 2D FWHM Raman maps acquired from 100 points covering a 40-80 μm^2 area of graphene films grown on Cu-Ni alloy substrates, of three

compositions, at 0.11 mbar growth pressure, 1000 °C and CH₄: H₂ gas ratio 2:1 by volume. The I_{2D}/I_G data, together with the 2D FWHM maps, confirms the dominance of FLG coverage over the surface of the Cu-Ni alloy. The I_{2D}/I_G values range ~ 0.4-0.6 for Cu70-Ni30 substrate, 0.2-0.4 for Cu55-Ni45 and 0.09-0.1 for Cu33-Ni67. Furthermore, the 2D FWHM ranges are ~ 40-60 cm⁻¹, 60-90 cm⁻¹ and ~40-45 cm⁻¹ for the Cu70-Ni30, Cu55-Ni45 and Cu33-Ni67 substrates respectively.

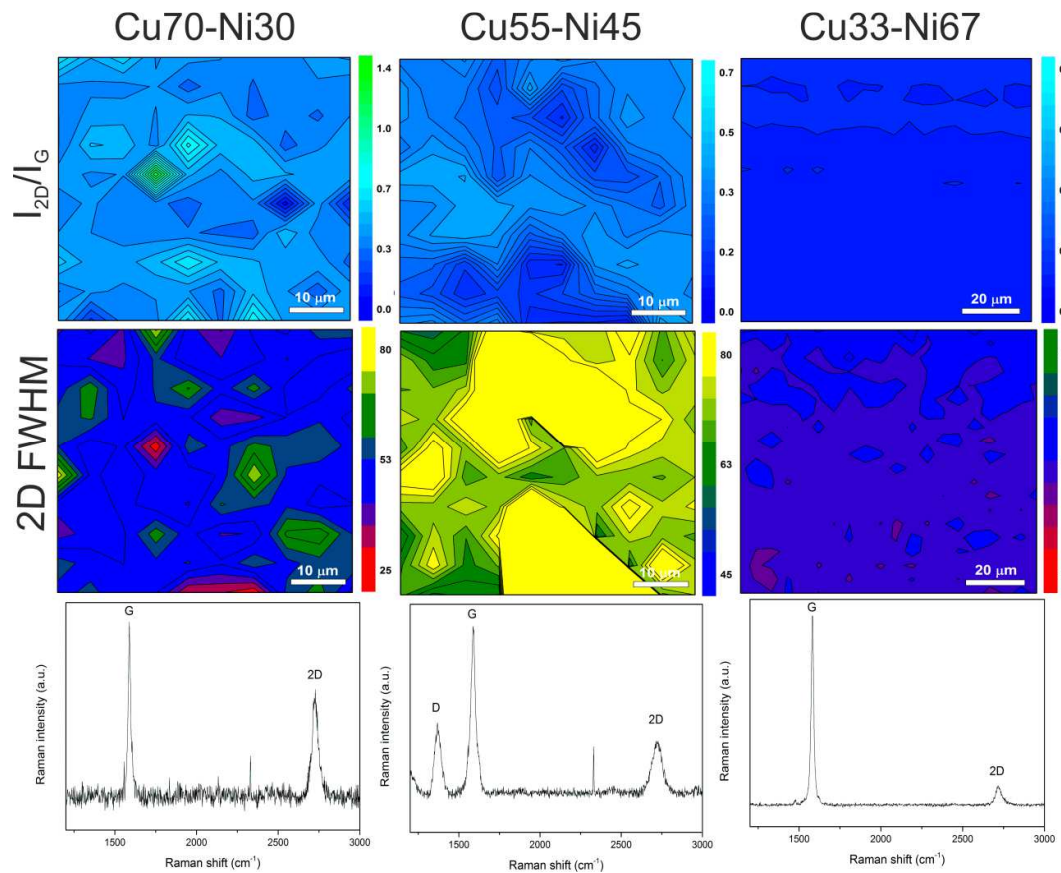


Figure 5. 3. Raman I_{2D}/I_G , 2D band FWHM and Raman spectrum for Cu-Ni alloys. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure and fast cooling rate.

The variation in the I_{2D}/I_G ratio between the three Cu-Ni alloy concentrations can be identified from the Raman spectra data in Figure 5.3. A relatively high D peak was observed in the Cu55-Ni45 spectrum, which is usually an indication of structure defects

and edges in graphene. However, no such bands were seen in the films grown on the Cu70-Ni30 and Cu33-Ni67 substrates.

A noticeable change in the I_{2D}/I_G ratio occurs when the growth pressure increases to 0.65 mbar. Looking at Figure 5.4, the values of the intensity ratio are ~ 0.45 -0.9, 0.2-1.3 and 0.5-0.9 for Cu70-Ni30, Cu55-Ni45 and Cu33-Ni67 substrates respectively. Graphene number of layers statistics, acquired from Raman spectroscopy results, are presented in Figure 5.5.

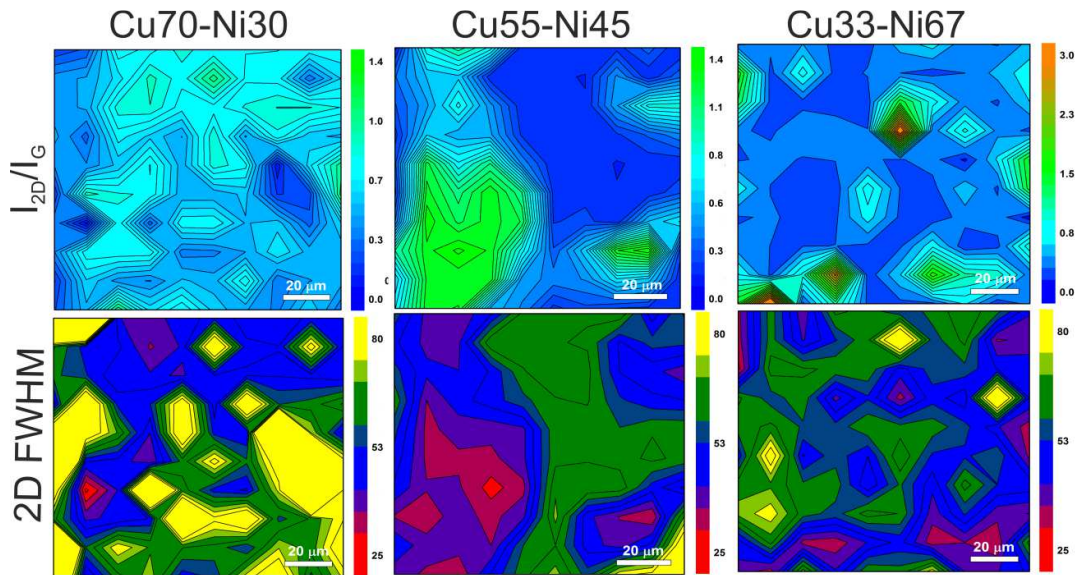


Figure 5. 4. Raman I_{2D}/I_G and 2D band FWHM Cu-Ni alloys. Growth conditions are 1000 °C growth temperature, 0.65 mbar growth pressure and fast cooling rate.

The effect of Ni content is noticeable on the graphitic film thickness. Moving from 0 % to 100 wt. % Ni, the coverage of BLG declines, while the coverage of FLG increases. The C solubility for the corresponding alloys is also included in Figure 5.5 for a better understanding of the results. The increase of C solubility that occurs with increasing Ni content is reflected by the increasing thickness of the graphene film. By increasing the solubility of C, the ability of the substrate to dissolve C into the bulk increases. In fact,

introducing Ni increases not only C solubility but also increases its catalytic activity towards hydrocarbon decomposition^{226,231}.

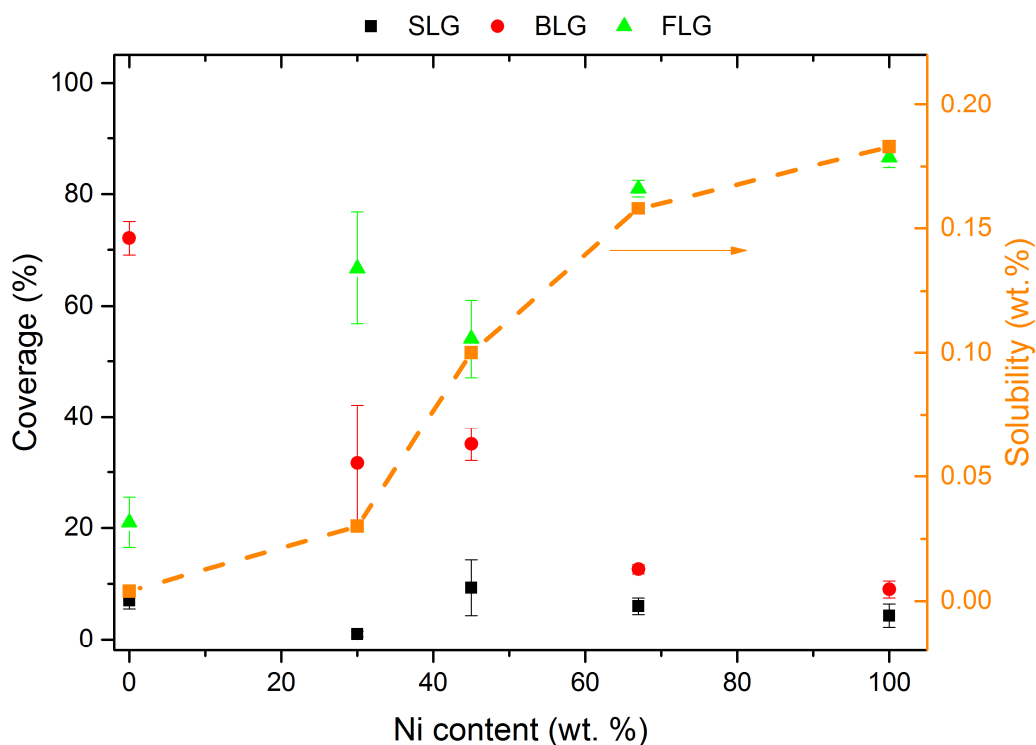


Figure 5. 5. Effect of Ni content on the thickness of CVD graphene. Coverage percentage of FLG increases with increasing Ni content in Cu-Ni alloy. A number of graphene layers coverage calculated based on Raman I_{2D}/I_G . The orange dash line represents the C solubility data. Growth conditions are 1000 °C growth temperature, 0.65mbar growth pressure and fast cooling rate.

Further evidence for the role of C solubility in controlling CVD graphene deposition is the influence of growth time. Figure 5.6 shows the time required to grow a graphitic film against Ni content and compares it with the experimental C solubility values for each alloy. It is clear that incubation time, which is the time elapsed before the appearance of graphene layers on the surface, increase by increasing carbon solubility of the Ni alloy. This observation is consistent with the proposed mechanism of CVD graphene growth on Cu-Ni alloy being a diffusion–precipitation process. When the hydrocarbon interacts with the metal surface, C is liberated from the hydrocarbon

structure due to breaking the C-H bond and hence the incubation time required for the C to diffuse into the alloy until it reaches a critical concentration or saturation^{93,245}.

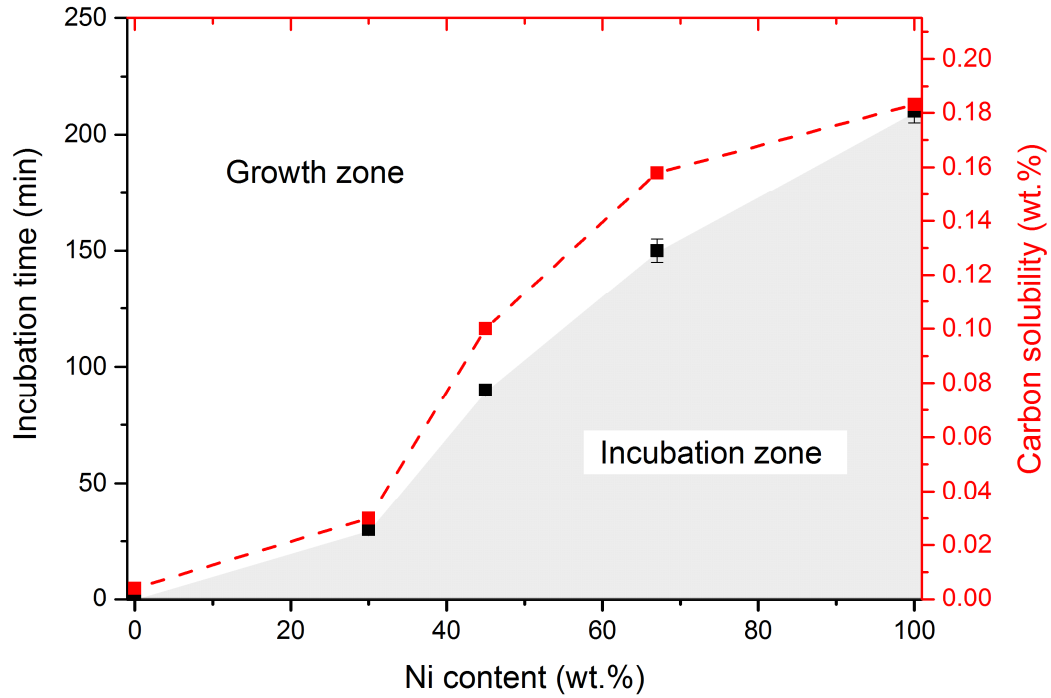


Figure 5. 6. Effect of Ni content on growth time. The area under the curve (grey shade) represents the incubation zone, which shows no growth on the surface. The blank white area is the growth zone where graphene starts to cover the metal surface. The red-dash line is the experimentally measured Cu-Ni C solubility values for correspondence alloy from ref.²³². Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure and fast cooling rate.

It is noticed that the trend of the growth time with respect to Ni content, is not changed by growth parameters, e.g. when the growth pressure is increased to 0.65 mbar the relative behaviour on each composition substrate does not change, even though the incubation time is reduced because of the high C concentration in the gas phase (Figure 5.7).

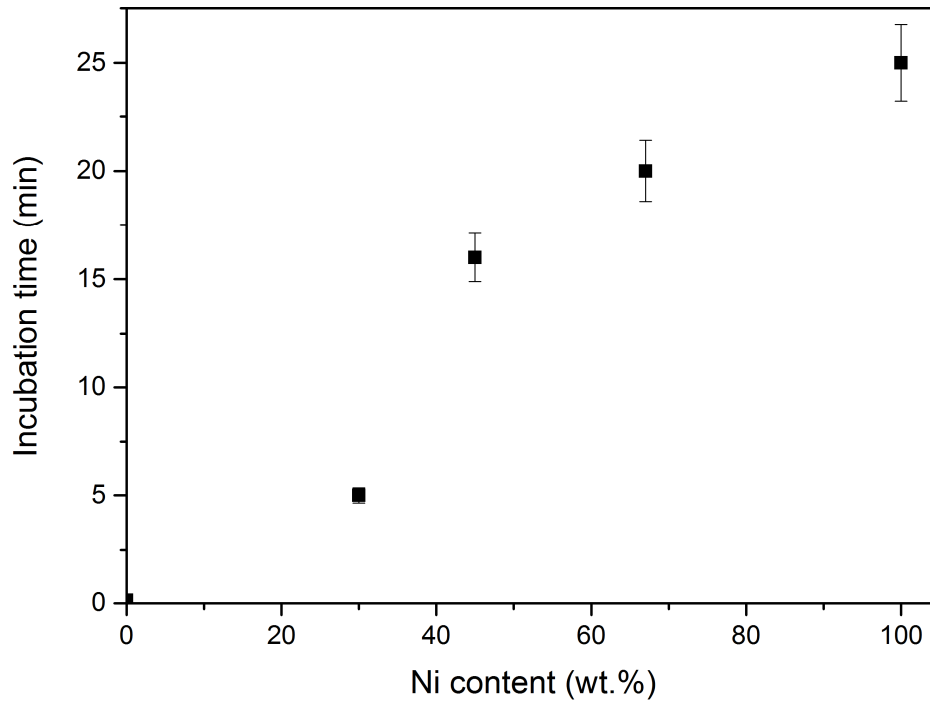


Figure 5. 7. Ni content in Cu-Ni alloy versus incubation time. Growth conditions are 1000 °C growth temperature, 0.65 mbar, growth pressure and fast cooling rate.

5.2.2. Effect of cooling rate

Cooling rate of the sample found to play a critical role in controlling the amount of C in the diffusion-precipitation process. As demonstrated for pure Ni substrates in chapter four, the amount of C precipitated on the surface increases if the C dissolved in Ni mixture cools down slowly. Growth conditions are the same as stated previously *i.e.* 0.11 mbar total pressure, 1000 °C growth temperature and 2:1 CH₄: H₂ gas ratio. The growth time is as presented in Figure 5.6 except for Cu when 30 mins were used. SEM images for CVD graphene grown under the same conditions but with different cooling rates show a clear diversity in terms of surface coverage (Figure 5.8).

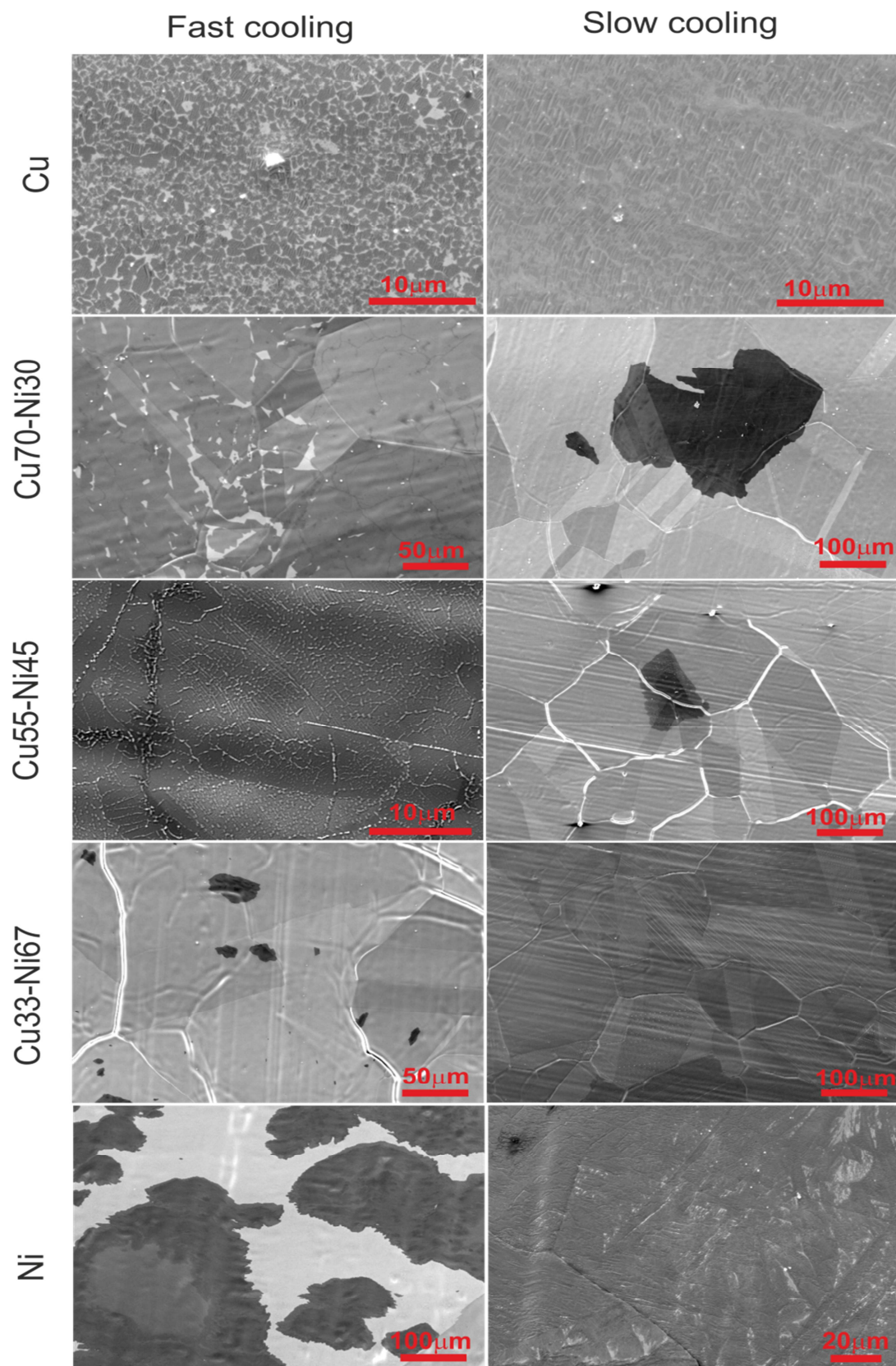


Figure 5. 8. SEM images panel demonstrates the effect of cooling rate on graphene coverage for different Cu-Ni alloy concentrations. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure and fast cooling rate. Growth time as presented in Figure 5.6.

The graphene surface coverage percentage was determined by using Image J (Java based image processing programme) to analyse the SEM images in Figure 5.8 for the Cu-Ni alloy substrates, as well as the pure metals. This data is plotted in Figure 5.9. Under fast cooling conditions, the graphene film shows a transition from high coverage with Cu-rich substrates to low coverage with Ni-rich compositions. However, during slow cooling conditions, the behaviour reverses with low graphene coverage on Cu-rich alloy substrates and greater coverage with Ni-rich alloys. CVD graphene coverage on pure metals (Cu and Ni) is also affected by cooling rate, however, the difference between slow and fast cooling rate is not so marked. In order to determine the reasons for this transition in behaviour with cooling rate, it is necessary to ascertain the composition of the alloy (Cu, Ni and C content) beneath the surface on which the graphene film is grown.

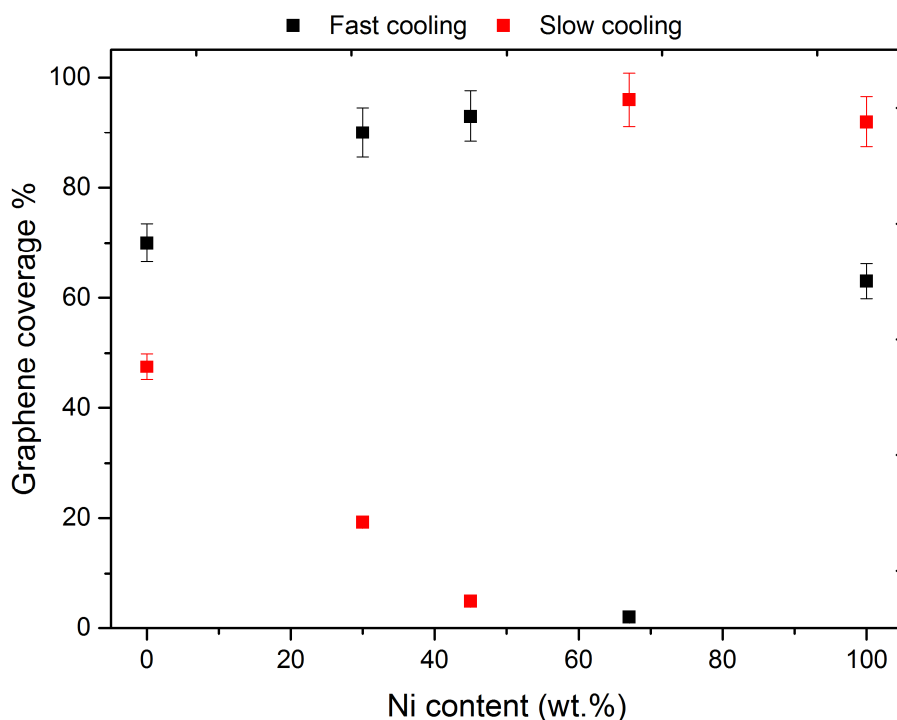


Figure 5. 9. Cu-Ni surface coverage at slow cooling rate 27 °C/min and fast cooling rate 376 °C. The calculation based on SEM images in Figure 4.8 using Image J software. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure and growth time as presented in Figure 5.6.

5.2.3. GDOES results

GDOES was used to carry out concentration-depth profile analyses. The advantages of using GDOES for depth profiling is its high processing speed (~ 1 min per one run), and the analysis depth range is a few micrometres, which is not easy to perform with other techniques such as depth profiling secondary ion mass spectroscopy (SIMS) ²⁴⁶. The sample to be analysed is mounted as a cathode in direct current plasma. Argon ion bombardment removes the sample surface atoms, which enter the plasma by diffusion. Characteristic wavelengths emitted from the excited atoms are recorded by the spectrometer. By sputtering layer by layer and recording the resulting wavelength signal, it is possible to measure the variation in alloy concentration using GDOES as a sample depth probe. The concentration of the selected element is proportional to the measured emission intensities, which expressed in equation 5.1²⁴⁷:

$$I_{\lambda(E)} = \alpha_{\lambda(E)} C_{E,M} \quad 5.1$$

where $I_{\lambda(E),M}$ is the intensity of the emission line of element E , $C_{E,M}$ is the concentration of the element and $\alpha_{\lambda(E)}$ is a constant. The constant is determined by calibration using standard samples with a known concentration of the element of interest; however, preparation of the standard sample is expensive. An alternative method is to use the as received Cu-Ni foils as a standard, although this reduces the absolute accuracy of the data. The correlation between sputtering time and sample depth was determined using optical profilometry to determine the sputtered depth. Thus, even if the intensity-sputtering time curve not converted to its equivalent concentration-depth scale, the variation in element line emission with respect to sputtering time can still provide important information about the relative concentration depth profile of the elements studied.

GDOES is a destructive analytical technique because etching the sample surface atoms forms a crater (Figure 5.10 (a)). Measuring the depth of the crater provides valuable information of how the concentration of the desired element changes with depth below the surface. Figure 5.11 shows the calculated sputtering rate for one of the Cu-Ni alloys used in this study. The sputtering rate for pure Cu is higher than that for pure Ni, which is in agreement with the work of Hirokawa et al²⁴⁸. However, the Cu-Ni alloys show different sputtering rate, with the highest value found for Cu55-Ni45 (Table 5.1).

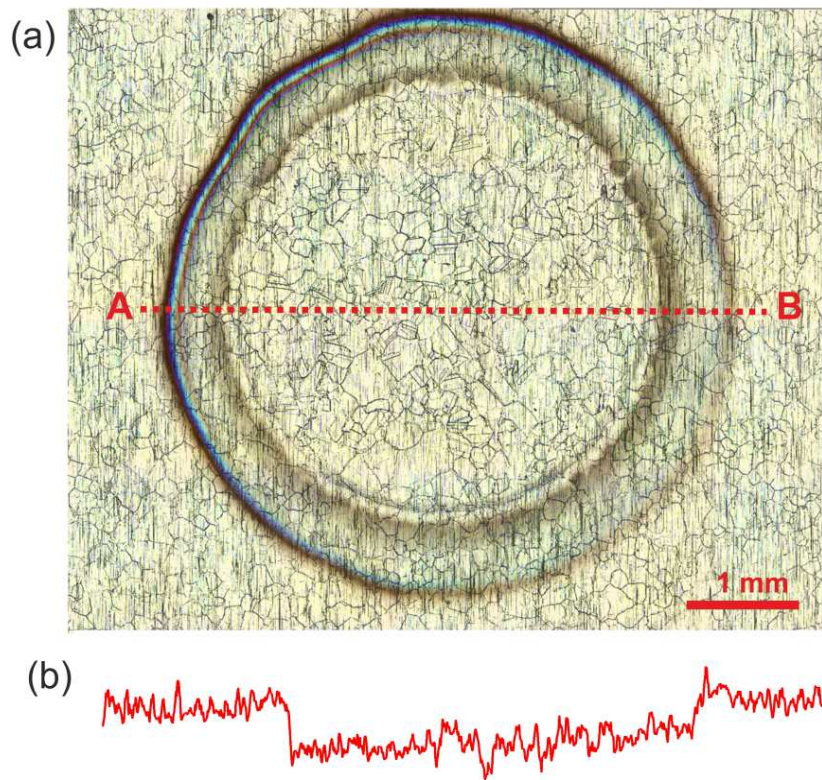


Figure 5. 10. (a) An optical-laser image of the crater created after 30 s depth profile measurement by GDOES for Cu33-Ni67 samples. (b) Crater depth through A-B line calculated by laser interferometry.

Table 5. 1. Sputtering rate for the Cu-Ni alloys used in this study calculated from crater depth measured by laser spectroscopy after 30 s sputtering time.

Ni content wt. %	Crater Depth (μm)	Sputtering Rate ($\mu\text{m/s}$)
0	4.83	0.161
30	4.99	0.166
45	5.10	0.170
67	4.86	0.162
100	4.32	0.144

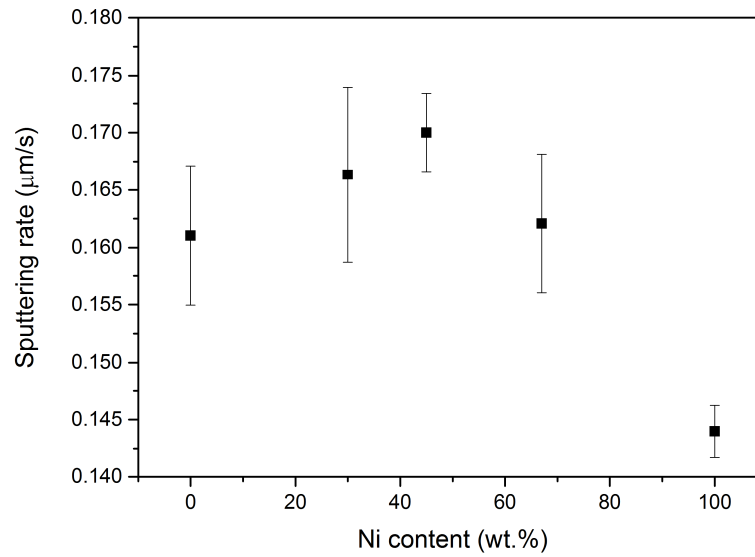


Figure 5. 11. Sputtering rate of Cu-Ni alloys, Ni shows the lowest value and the Cu55-Ni45 shows highest. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure and fast cooling rate

Figure 5.12 showing the sputtering time-intensity profile for the three elements; Cu, Ni and C beneath the CVD graphene film grown on Cu-Ni using fast and slow cooling rates. There is a clear difference between the profiles obtained at the different cooling rates. After fast cooling rates, the profile shows stable and smooth plasma intensity for both Cu and Ni, except at sputtering time < 2 s, where the emission lines intensity increase, which is attributed to the influence of the free surface²⁴⁹. The depth profiles obtained after slow cooling shows an interesting change in the recorded intensity. For

Cu70-Ni30 substrates, at sputtering time 2.5 s indicating a depth just below the surface, the Cu intensity decreases and the Ni intensity increases significantly. However, after 10 s the Cu and Ni intensities revert back to the stable and parallel profile seen with rapid cooling. However, this effect decreases as the Ni content of the alloy increases: with the Cu55-Ni45 substrate, the Ni intensity peak is broader, and the Ni-rich alloy (Cu33-Ni67) shows almost stable Cu and Ni plasma intensities over the measured depth for both cooling rates.

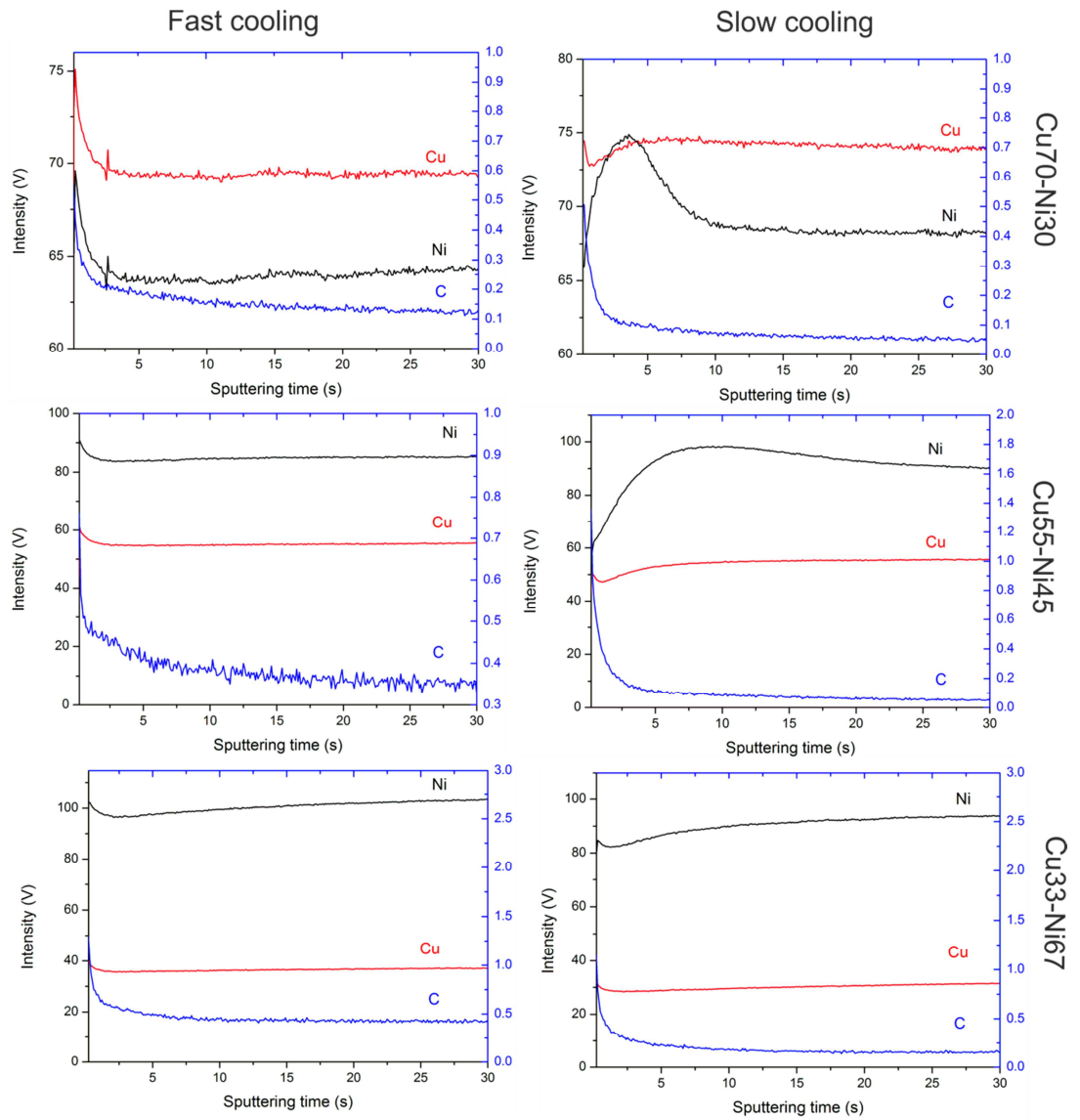


Figure 5. 12. GDOES intensity-sputtering time profile for Cu, Ni and C in Cu-Ni alloys at slow and fast cooling rate. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure and growth time as stated in Figure 5.6.

The change in Ni plasma intensity near the surface with the highest Ni content substrate is very small, and for Cu, it is not detectable. The GDOES composition depth profile data from the Cu-Ni alloys is summarised as follows:

1. The plasma intensity of Cu and Ni at the surface is always higher than the bulk (the flat intensity region) regardless of the cooling rate.
2. After fast cooling rates, the plasma intensity profile is smooth and flat for both Cu and Ni signal.
3. Slowly cooled samples exhibit disturbances in Cu and Ni intensity at the surface and subsurface, indicating a local change in alloy composition.
4. The intensity/composition changes with Ni content, *i.e.* it is more obvious for the Cu₇₀-Ni₃₀ substrate alloy than for Cu₃₃-Ni₆₇.

The gradual increase in GDOES intensity near the surface for both Cu and Ni has been reported previously for Cu-Ni alloys; this is believed to be due to the change in the Cu-Ni composition close to the free surface^{249,250}. The change in surface and subsurface composition of Cu-Ni alloy has been studied experimentally and theoretically, with the results confirming that the Cu-Ni alloy surface is always Cu-rich^{251–253}. Figure 5.13 shows Cu-Ni alloy bulk vs surface composition at different temperatures collected from literature; it is clear from Figure 5.13 that the Cu-Ni alloy surface is Cu-rich due to Cu segregation. Moreover, the concentration of Cu at the alloy surface is influenced by both the working temperature and the bulk alloy concentration (Figure 5.14). However, these studies of the Cu segregation phenomena in Cu-Ni mixture were all performed under atmospheric conditions.

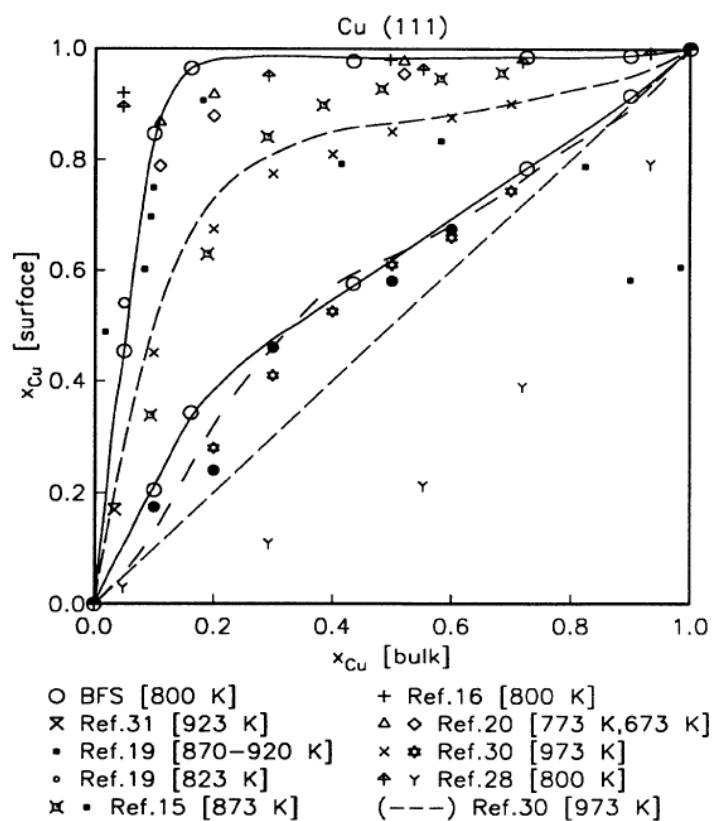


Figure 5. 13. Cu-Ni surface composition vs bulk composition showing segregation of Cu at the surface. Figure from ²⁵³.

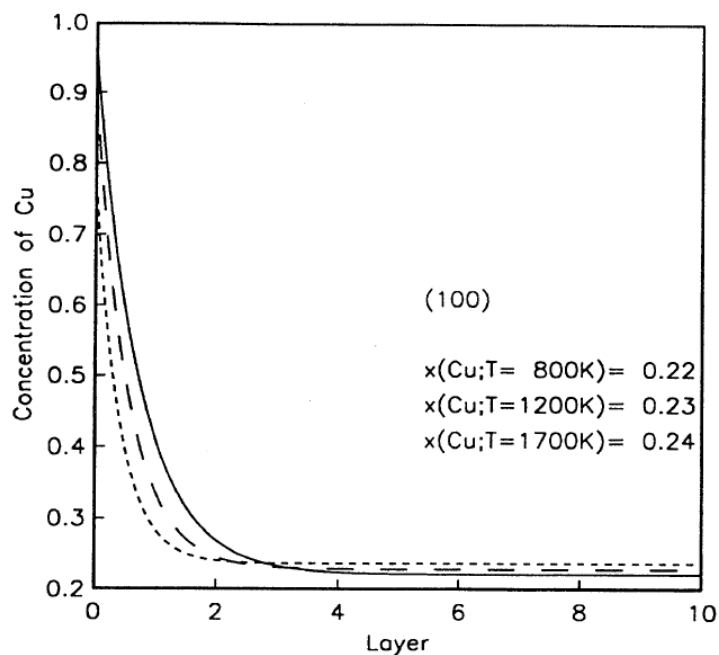


Figure 5. 14. Cu(100) depth profile of different bulk concentration and temperature. Figure from ²⁵³.

In low-pressure CVD conditions, during annealing and growth at 1000 °C, Cu evaporates from the alloy surface, due to the proximity of the working temperature to the Cu melting temperature (1084 °C). The low background pressure (0.11 mbar) also further facilitates Cu evaporation. Therefore, the concentration of Cu at the surface decreases. However, the simultaneously Cu diffusion from bulk to the Cu depleted surface occurs to keep the system equilibrated. Therefore, when the growth terminates and the sample cools down at a fast cooling rate (~ 376 °C/min) the GDOES depth profile for all the three samples is flat and steady which reflects composition homogeneity.

Time is an important parameter to achieve segregation equilibrium; this is simply demonstrated by the approximate solution of diffusion equation²⁵⁴:

$$c^{\emptyset} = 2c^B \sqrt{\frac{Dt}{\pi}} \quad 5.2$$

where $c^{\emptyset}$ and c^B are concentrations at the surface (in cm⁻²) and bulk (in cm⁻³) of the segregated atom, D is the interdiffusion coefficient of an atom and t is the segregation time. Therefore, according to equation 5.2, because the composition change is proportional to the square root of the elapsed time, the characteristic composition will be a function of cooling rate and at high cooling rates sample homogeneity is not achieved. Interdiffusion coefficient (D) of the segregated element has a significant influence because it determines how fast the atom diffuses in the alloy. For Cu in Cu-Ni alloys, it is found that the diffusion coefficient of Cu reduces with increasing Ni content^{255–257}, (Figure 5.15).

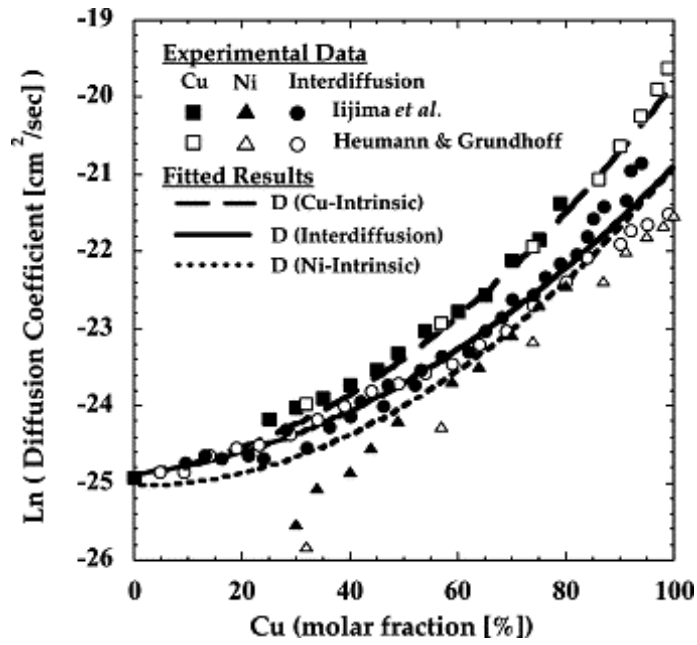


Figure 5. 15. Calculated Cu-Ni interdiffusion at 1000 °C, the interdiffusion decreases with increasing Ni content x in the alloy composition. Figure from ²⁵⁵.

The C depth profile for all Cu-Ni alloys in this study shows higher bulk intensity at fast cooling rates compared with the slow cooling rate, Figure 5.12. This may be due to short C segregation time during cooling rate. Moreover, there is an increase in C signal intensity with respect to Ni content also observed Figure 5.16, where the C signal is compared for all the substrates studied. For the purpose of a deep investigation of the relationship between the incubation time and the C content in the substrate, the C intensity at sputtering time 30 s (which is far from the substrate surface) is plotted against the Ni content for both fast and slow cooling rate in Figure 5.17. This shows that the fast cooled samples have C contents in accordance with the reported C solubility of the alloy. However, the C intensity difference is considerable between fast and slow cooled samples, with the C content of the slow cooled samples being significantly lower than the solubility limit.

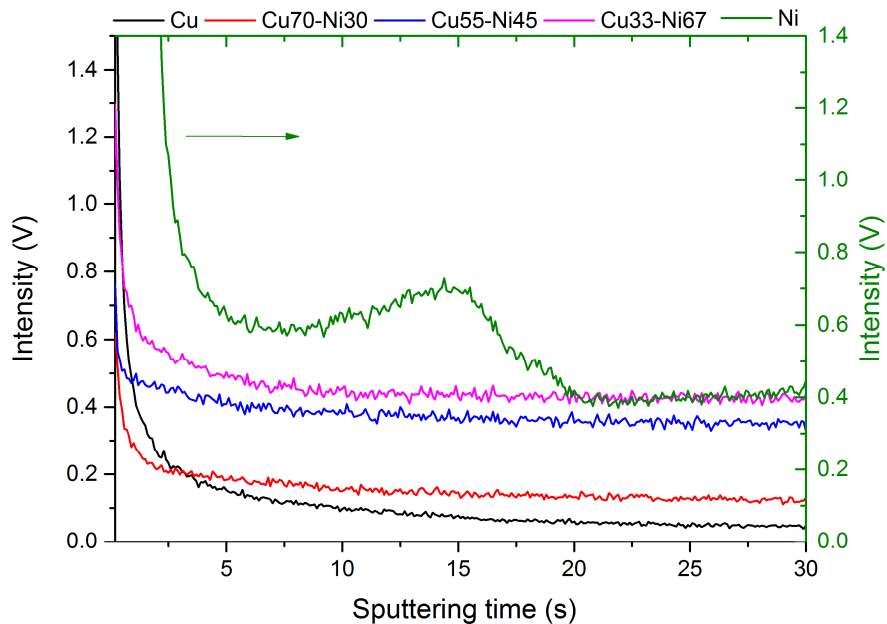


Figure 5. 16. GDOES C intensity-sputtering time profile in Cu-Ni alloys. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure, fast cooling rate and growth time as stated in Figure 5.6.

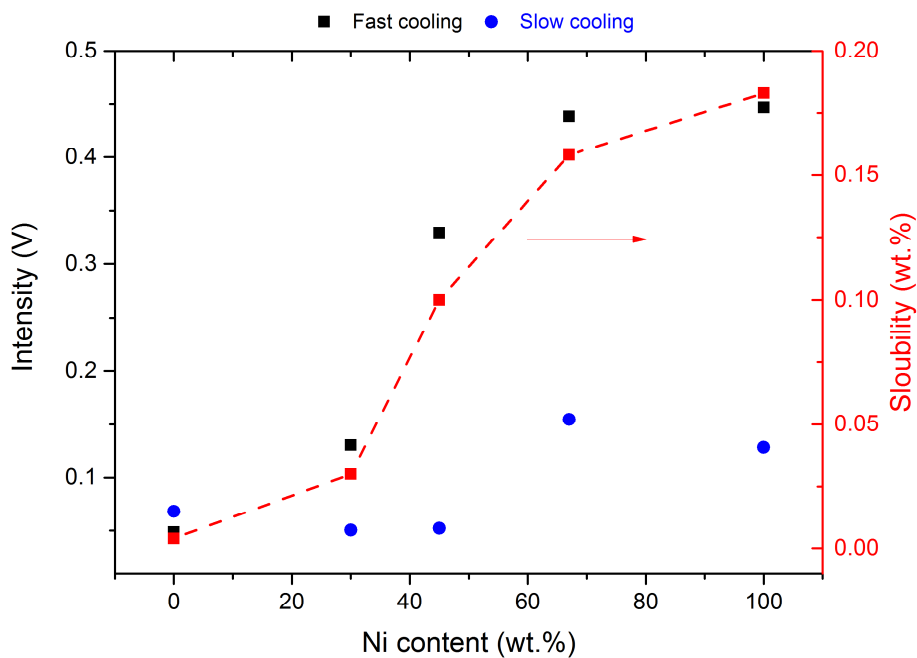


Figure 5. 17. GDOES C intensity versus Ni content for fast and slow cooled samples. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure and growth time as stated in Figure 5.6.

The data shown in Figure 5.17 agrees with the proposed diffusion-perspiration mechanism for Cu-Ni alloy substrates. The C solubility limit represents the quantity of

C that diffuses into the substrate during the incubation time. When the maximum solubility concentration is achieved growth of graphene on the surface is possible. If the sample is cooled down fast, then the amount of C that can diffuse back to the surface is small, however, at the slow cooling rate, the substrate remains at an elevated temperature sufficiently long to allow C to diffuse towards the surface. The difference in composition between the surface, subsurface and the bulk of Cu-Ni alloy leads to change in C solubility and diffusivity within the same substrate. Consequently, a diffusion barrier might be developed, preventing the segregation of C from the bulk towards the surface under same conditions, possibly explaining the low graphene coverage observed at the slow cooling for Cu70-Ni30 and Cu55-Ni45 substrates.

5.3. Conclusion

CVD of graphene on Cu-Ni alloy substrates shows an intimate relationship between the film thickness and the Ni content. With increasing Ni content, the percentage of FLG, coverage increases and reaches full FLG coverage for 100 % Ni. This is attributed to the increase in C solubility with increasing Ni content. The substrate surface coverage is highly affected by the sample cooling rate after growth. Cu-rich substrates require fast cooling to achieve a good surface coverage; on the other hand, slow cooling is needed for Ni-rich substrates. The GDOES results reveal that the subsurface region of the Cu-rich substrate shows a change in composition, with an increase in Ni concentration, which might develop a diffusion barrier against C precipitation to the surface. The trend of C intensity of the region far from the surface of the fast cooled samples, replicate the C solubility trend. The C intensity of slowly cooled samples is much less than the fast cooled one, which is due to short precipitation period compared with the slow cooling rate.

6. CVD process simulation

6.1. Introduction

This chapter is dedicated to the simulation of the CVD growth of graphene. The simulation includes fluid flow dynamics, heat transfer and gas phase chemistry for the CVD reactor. Fluid flow calculation is essential in CVD because it indicates how the velocity and pressure are distributed in the CVD chamber, which significantly affects the CVD kinetics. Heat transfer was included because it has a significant influence on the fluid flow calculations. For example, the density of gases changes with temperature which results in a sequence changes of the velocity of gases, furthermore to visualise the temperature uniformity distribution within the CVD reactor. By combining results of the fluid flow and heat transfer calculations, the residence time could then be calculated.

The simulation performed by COMSOL Multiphysics 5.2a, which is a simulation software with the ability to solve different physical problems based on finite element analysis (FEA)²⁵⁸. FEA is a numerical method presented for the first time in 1956 to solve partial differential equation problems. It is mainly used to address the problems in heat transfer; structural engineering, fluid mechanics, aerodynamics, and electrostatics by dividing the system into small elements described by partial differential equations that are connected to each other by nodes which enable an approximate solution of the problem to be obtained²⁵⁹.

CVD graphene on Cu-Ni alloy is a catalytic growth process, *i.e.* the reaction between the precursor gas and the substrate surface governs the film growth. Therefore, investigating of this part of growth is based on results of the gas phase chemistry modelling. The importance of gas surface reaction calculation is to indicate the carbon

surface concentration. For the next section, the simulation methodology and results will be presented in detail, and it will be covering the following topics: thermodynamics, fluid flow, heat transfer, kinetics of gas phase reactions and kinetics of surface reactions.

6.2. Thermodynamics

In any CVD system, the thermodynamic analysis should be initially considered as it is vital step in determining whether the reaction of interest can take place or not at the given temperature and pressure. The Gibbs free energy of the reaction is the essential parameter, the more negative value, the more feasible the reaction to happen, with any positive energy meaning that the reaction cannot occur⁷⁸.

MTData was used, which is a thermodynamic software package developed by National Physical Laboratory (NPL). MTData is a single computer program based on Fortran code and calculates the equilibria of a given multicomponent system using Gibbs energy minimisation²⁶⁰. The software can calculate the phase equilibria of C_1 and C_{12} hydrocarbons and has 185 species in its database. Figure 6.1 showing the thermodynamic calculation results of 2:1 by volume CH_4 and H_2 gas mixture under 0.11 mbar and temperature range 25 - 1200 °C. CH_4 starts to crack at ~ 250 °C, leading to an increase in H_2 concentration, and reaches its equilibrium concentration at ~ 450 °C. However, CH_4 continues to decompose with increasing temperature and reaches its lower value at 1200 °C. C_6H_6 is present between 300-800 °C and vanishes at > 1000 °C. At the growth temperature (1000 °C) the most stable and dominant active species is C_2H_2 followed by C_4H_2 . At ~ 600 °C the gas phase contains CH_4 , C_6H_6 , C_2H_2 and C_2H_4 . All these hydrocarbons are known to be able to grow graphene at low temperatures^{96,202,261,262}, however experimentally at this temperature, no graphene was

observed on the Cu-Ni substrates with graphene been seen on Cu at temperatures ≥ 900 °C in both this study (Figure 4.13) and Lewis et al work.¹¹⁶

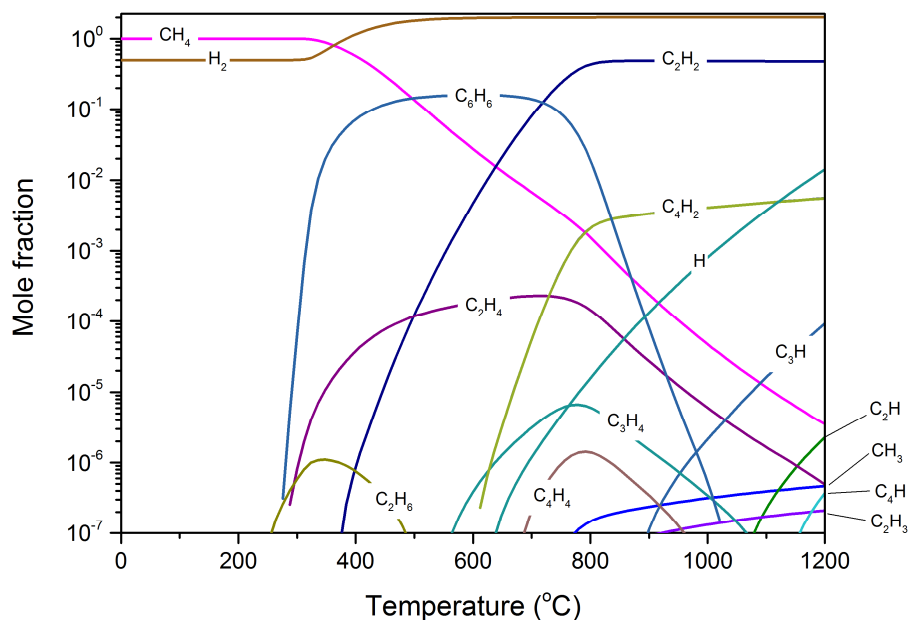


Figure 6. 1. Gas phase composition over a range of temperature at 0.1 mbar pressure calculated using MTDData. The calculation omitted solid carbon from the gas composition as it is assumed that graphene growth is a surface process.

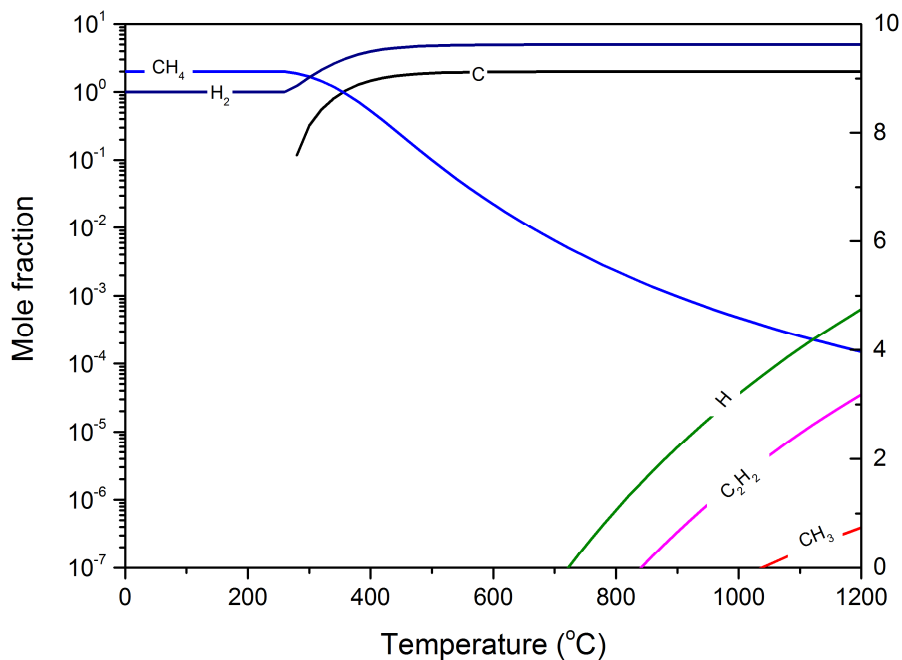


Figure 6. 2. Gas phase composition with solid carbon included in the thermodynamic calculations. The only significant gaseous species besides CH_4 and H_2 are H , C_2H_2 and CH_3 .

The thermodynamic calculation in Figure 6.1 omitted solid C, however, if C is included in the calculation, all the active hydrocarbons vanish excluding C_2H_2 and CH_3 . The solid C deposit starts to show at $\sim 300^\circ C$ and equilibrated with the gas phase at $\sim 500^\circ C$, Figure 6.2.

Based upon the thermodynamic results (Figure 6.1), the carbon supply to the substrate from the gas phase is not provided just by CH_4 but there are also a contribution from other species which have a higher C: H ratio than CH_4 (e.g. C_2H_2 and C_4H_2). The difference in the chemical potential between the C in the gas phase (Figure 6.1) and C chemical potential above the substrate surface (Figure 6.2) is the driving force for growth, and can be calculated by^{263–265} :

$$\Delta\mu = -RT \ln \left(\frac{P_C}{P_C^f} \right) \quad 6.1$$

Where P_C is the partial pressure of C in the gas phase and P_C^f is the equilibrium vapour pressure of the solid.

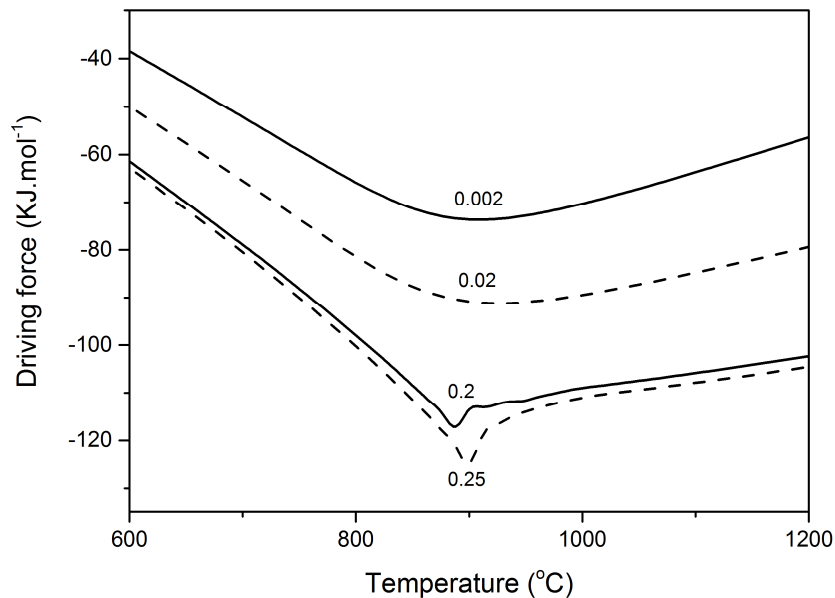


Figure 6. 3. Driving force for deposition versus temperature for R_{CH} 0.002, 0.02, 0.2 and 0.25.

Figure 6.3 showing the driving force of graphene growth calculated for four R_{CH} , 0.002, 0.02, 0.2 and 0.25. The driving force is sensitive to C concentration in the feedstock, at high C content the possibility of growth is high, while at low C content the possibility is low because the etching by H is high. At R_{CH} 0.2 it seems that at ~ 900 °C the growth driving force reaches its maximum value and deposition is most likely.

The deposition of the graphitic film in a typical temperature and pressure is, in fact, a competitive reaction process between three elements, C, H and O ²⁶⁶. At high H concentration, the lifetime of the unstable surface C deposit is short due to etching by H atoms ¹⁰⁷. However, a C rich gas mixture gives a thick and defective graphitic film ²¹⁶. It is found that adding O to the C-H mixture can hinder the growth process due to the formation of CO or CO₂. The source of O in CVD reactor is typically the residual O from the substrate ²⁶⁷, and from the atmosphere (even if the system is working under low pressure there is residual O ²⁶⁸).

Therefore it would be useful if the boundaries of CVD graphene in equilibrium with C-H-O gas phase composition could be determined. Figure 6.4 is the C-H-O phase diagram constructed based on Bachmann rule ²⁶⁹. Each side of the triangle represents the atomic fraction of the binary system in the gas composition, *i.e.* O-C, C-H, and H-O. All the points in the phase diagram are experimental work collected from literature of CVD graphene which combined with experimental work of CVD of diamond collected by Bachmann. The C-H-O phase diagram divided into three regions, the diamond growth region which is lying in the CO line. This region identified by Bachmann based on the CVD of diamond experimental work. The diamond growth region split the C-H-O phase diagram into two halves, the lower half where no graphene or diamond grow. The upper half is the graphene growth region, which its boundary laying in C-H axis and starts from $X_H = 0.33$, which belongs to CVD of graphene using aromatic

hydrocarbon ($C_{24}H_{12}$)²⁷⁰, this is the lowest H fraction reported for CVD graphene, and ends at $X_H = 0.9996$ which is the highest H fraction reported which characterise by no graphene growth.

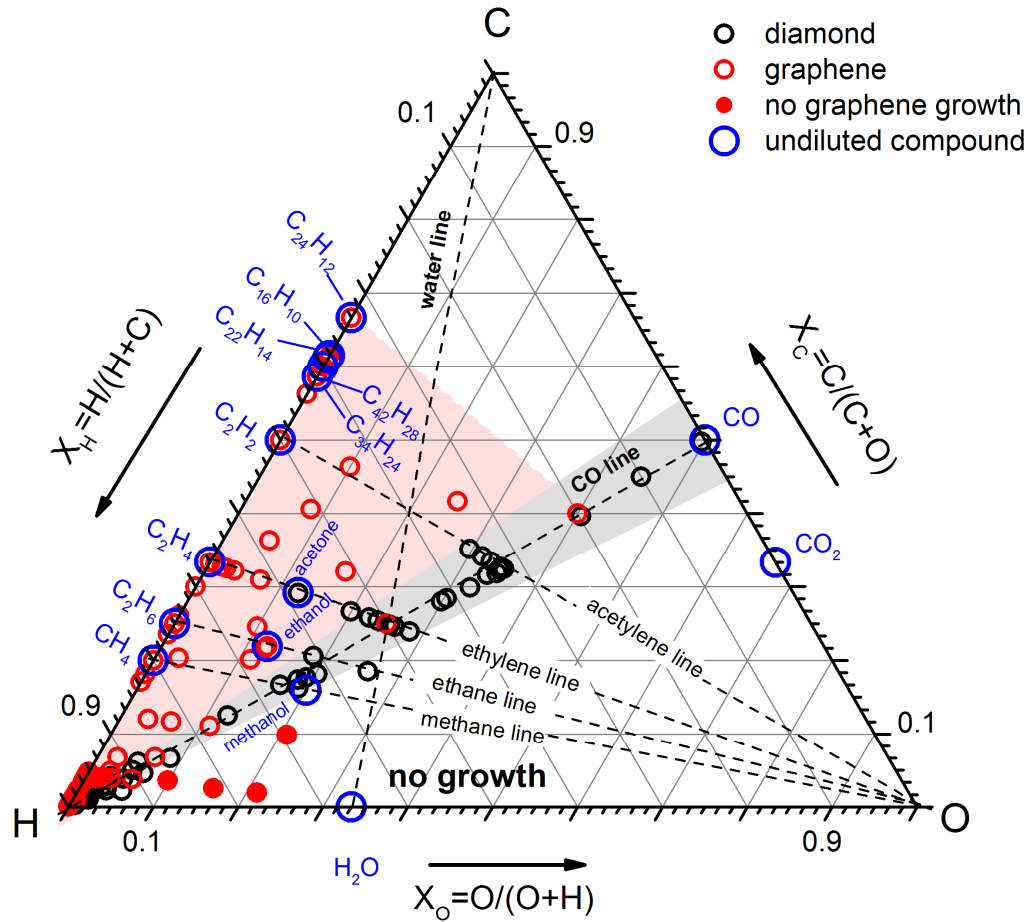


Figure 6. 4. C-H-O ternary phase diagram of CVD of diamond which is updated to CVD graphene. The open black circles are experimental data for CVD diamond collected by Bachmann²⁶⁹. The red open circles are CVD graphene data from literatures^{86,92,95,107,145,203,204,208-214,218,271-275}. The open blue circles are undiluted compounds. The solid red circles for no graphene growth. The grey shaded area is the CVD diamond regions, and the light red shaded area is the CVD graphene region.

The highest reported fraction of O which successfully shows graphene growth by CVD is $X_O = 0.4$ ²⁷⁶ where the data point is lying on the CO line.

The use of O in the CVD gas phase composition shows unexpected enhancement due to the strong tendency of O to react to C which thermodynamically is favourable and leads to etching of carbon and controlling the growth rate²⁷⁷.

Figure 6.5 shows an enlargement of the C-H-O corner, in this small region especially between $X_H = 0.98$ and 0.9996 is preferred to graphene growth. This is because using a high fraction H prevents the formation of C in the gas phase and hence avoids snowing in the reactor.

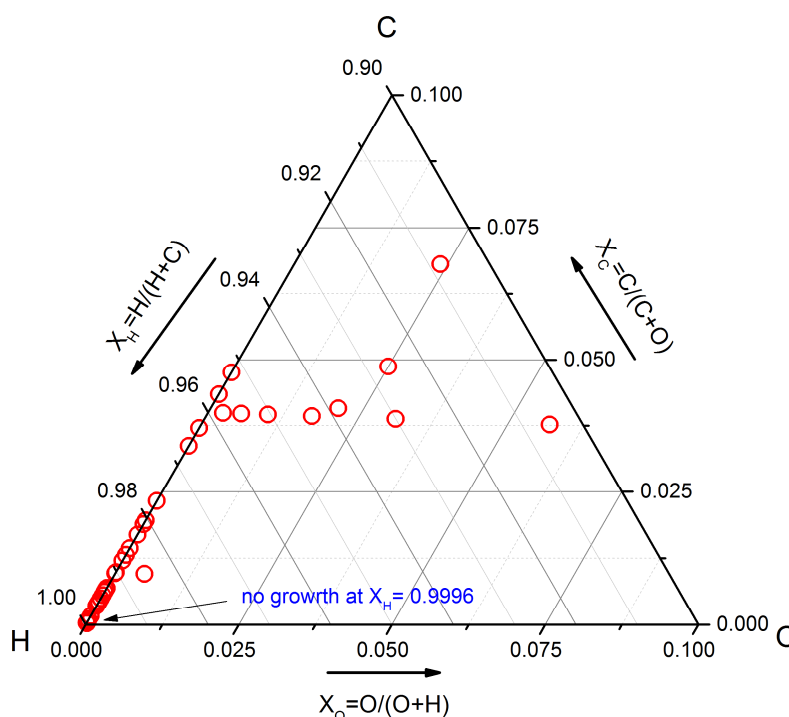


Figure 6. 5. Enlarge of the H rich corner of the C-H-O phase diagram. At H:C ratio 0.9996 no graphene growth recorded.

The C-H-O phase diagram gives the limits of CVD graphene which is useful in mapping future work. As stated earlier, the thermodynamic calculation is an essential step in CVD process, however, it has a limitation: firstly, the calculations assume that the system is under thermodynamic equilibrium, therefore the software based on the embedded database predicts products which experimentally are not found, such as C_{60} ,

diamond and liquid hydrocarbon. The user omits the unnecessary product depending on his/her experimental knowledge which creates uncertainty in the reported calculation. The second limitation, it is difficult to calculate the deposition rate of the solid film under consideration, because the rate is primarily determined by chemical kinetics. Therefore, kinetics calculation is urgently needed to calculate the growth rate.

6.3. Fluid flow and heat transfer

6.3.1. Setting COMSOL Multiphysics

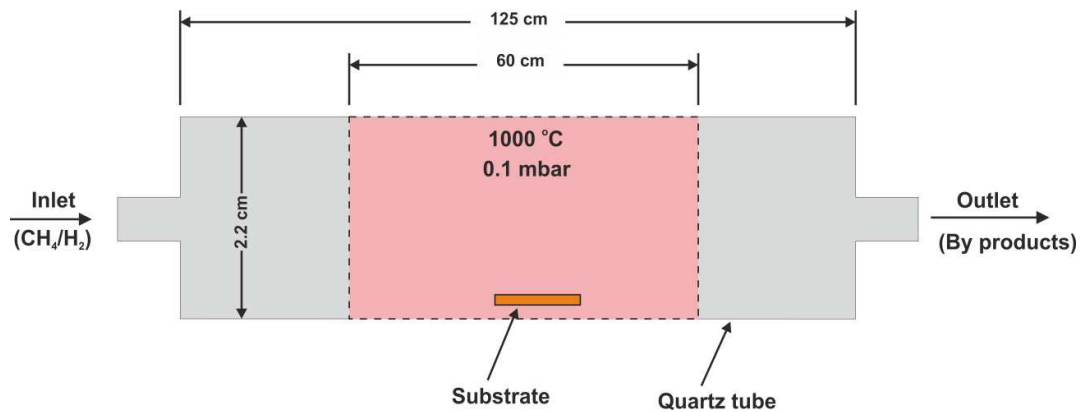


Figure 6. 6. Sketch drawing shows the CVD reactor geometry with it operation conditions. The reactor is 125 cm long and 2.2 cm diameter, the red shaded area represent the isothermal zone of the reactor which is 60 cm long and heats up to 1000 °C. The grey shaded areas are the cold zones which subjected to natural convection. The substrate position in the middle of the isothermal zone and the system is working under 0.1 mbar growth pressure. The reactant gases introduced to the system through the inlet and leave the chamber under the rotary pump action.

Figure 6.6 shows a 2-D schematic diagram of the working conditions of the CVD reactor to be modelled. The reactor is 125 cm in length and 2.2 cm in diameter with a 60 cm length heating zone at 1000 °C. The reactor has an inlet point, where the gas mixture is introduced to the system, and an outlet point connected to a mechanical pump which brings down reactor pressure to 0.1 mbar. The metal substrate (1×1 cm) located in the

middle of the heating zone and the gap between the bottom surface of the substrate and the quartz wall is ~ 3 mm. Moreover, the two parts of the quartz tube laying outside the heating zone subjected to natural convection with the laboratory atmosphere.

Based on this sketch, the 2-D space COMSOL geometry of the model is built including the real reactor dimensions and working conditions.

The next step after building the geometry is meshing, *i.e.* breaking down the geometry into nodes. The geometry meshed to 55819 elements of four different types, triangular, quadrilateral, edge and vortex, Figure 6.7.

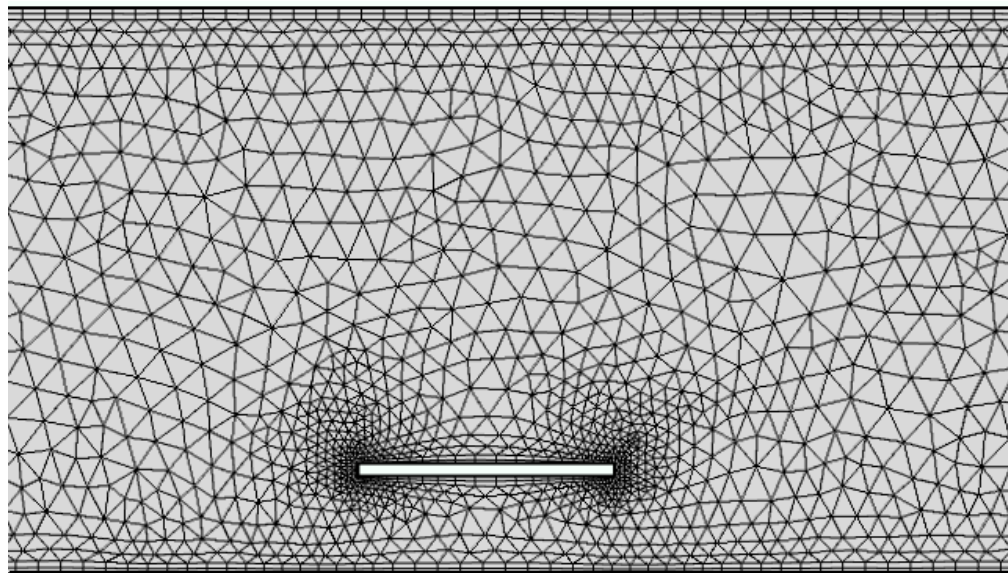


Figure 6. 7. Image snapshot of the middle of the isothermal zone after the geometry meshing process. The total number of elements is 55528 divided by 49696 triangular elements, 5835 quadrilateral elements, 2964 edge elements and 12 vertex elements.

Fluid flow and heat transfer interfaces coupled to a non-isothermal flow Multiphysics interface, because according to ideal gas law, gas properties affected by temperature¹⁰⁹. By using this modelling environment embedded in COMSOL, it is possible to visualise the change in gas properties when temperature change.

The fluid flow interface in COMSOL based on Navier-Stokes equations which in this work take the form ²⁷⁸:

$$\rho(u \cdot \nabla)u = \nabla \cdot \left[-pI + \mu(\nabla u + (\nabla u)^T) - \frac{2}{3}\mu(\nabla \cdot u)I \right] + F \quad 6.2$$

where:

ρ is the density (kg/m³), u is the velocity vector (m/s), p is the pressure (Pa), F is the volume force vector (N/m³), T is the absolute temperature (K), μ is the dynamic viscosity (Pa.s) and I is the identity matrix.

The heat -transfer and fluid interface in COMSOL based on the flowing equation:

$$\rho C_p \left(\frac{\partial T}{\partial t} + (u \cdot \nabla)T \right) = -(\nabla \cdot q) + \tau : S - \frac{T}{\rho} \frac{\partial \rho}{\partial T} \bigg|_p \left(\frac{\partial p}{\partial t} + (u \cdot \nabla)p \right) + Q \quad 6.3$$

Where:

ρ is the density (kg/m³), C_p is the specific heat capacity at constant pressure (J/kg.K), T is absolute temperature (K), u is velocity vector (m/s), q is heat flux by conduction (W/m²), p is pressure (pa), τ is the viscous stress tensor (pa), S is strain-rate tensor (1/s) and Q contains heat sources other than viscous heating (W/m³). S is given by:

$$S = \frac{1}{2} (\nabla u + (\nabla u)^T) \quad 6.4$$

The fluid input parameters are calculated for a CH₄/H₂ gas mixture using equations (6.5)-(6.8) ²⁷⁹ for the same mixing ratio stated in the experimental chapter (CH₄ and H₂ 2:1 by volume respectively). The specific heat at constant pressure and volume, C_p , C_v , are calculated by equation 6.5.

$$C_{y-mix} = \frac{x_1 C_{y1} + x_2 C_{y2}}{x_1 M_1 + x_2 M_2} \quad 6.5$$

Where C_y is the specific heat to be calculated *i.e.* C_v or C_p , M and x is the molecular weight and mole fraction of the pure gas respectively. The density of the gas mixture is presented in equation 6.6.

$$\rho_{mix} = x_1\rho_1 + x_2\rho_2 \quad 6.6$$

The thermal conductivity and the viscosity of the mixture, k_{mix} and μ_{mix} respectively, are estimated by equation 6.7.

$$y_{mix} = \sum_{i=1}^n \frac{x_i y_i}{\sum_{j=1}^n x_j \phi_{y,ij}} \quad 6.7$$

Where y_{mix} is the properties to be calculated (k_{mix} or μ_{mix}), $\phi_{y,ij}$ is a dimensionless constant which is given by equation 6.8.

$$\phi_{y,ij} = \frac{1}{2\sqrt{2}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{y_i}{y_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad 6.8$$

The required input mixture properties are listed in Table 6.1. The physical properties values of gas mixture were entered into the model as an equation with respect to temperature to enable the model to work with heat transfer consideration over a range of temperature.

Table 6. 1. Gas mixture properties, all the listed values are calculated for 2:1 CH₄: H₂.

Property	Symbol	Unit	Value
Dynamic viscosity	μ	Pa.s	$(-2 \times 10^{11})T^2 + (6 \times 10^{-8})T + (3 \times 10^{-6})$
Ratio of specific heat	γ	-	1.335
Heat capacity	C_p	J/(kg.K)	$-0.0008T^2 + 4.2083T + 1783.5$
Density	ρ	kg/m ³	$0.01114P_A/8.1225T$
Thermal conductivity	k	W/(m.K)	$(-3 \times 10^{-8})T^2 + (0.0006)T + 0.0309$

For the metal substrate and quartz tube, the physical properties are assigned from COMSOL materials library itself.

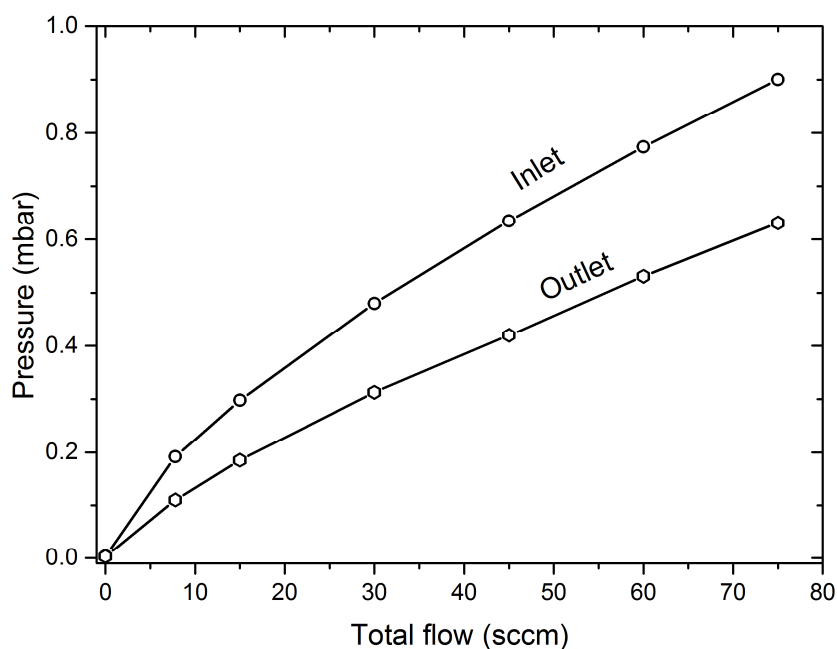


Figure 6. 8. The difference in pressure between the inlet and outlet of the CVD reactor. The pressure measurement performed under a flow rate range 0-75 sccm of CH₄ and H₂ with a mixing ratio 2:1.

The heat transfer in fluid Multiphysics calculation starts from the inlet point all the way through the outlet point; however, it needs a reference temperature and reference pressure to start with. The pressure of CVD reactor is measured for both the inlet and outlet ends, which have a different flow rate, Figure 6.8, the difference in pressure is obvious between the two ends. The reference temperature set at 25 °C, which is the inlet temperature, and the reference pressure is the inlet pressure at a total gas flow rate for experiment under study.

6.3.2. Results

Figure 6.1 shows the gas velocity distribution in the inlet point, the gas mixture travel inside the feeding pipeline at a velocity ~ 6 m/s under the experiment working pressure. The gas velocity reduced to ~ 2 m/s when enters the quartz tube due to expansion in gas volume.

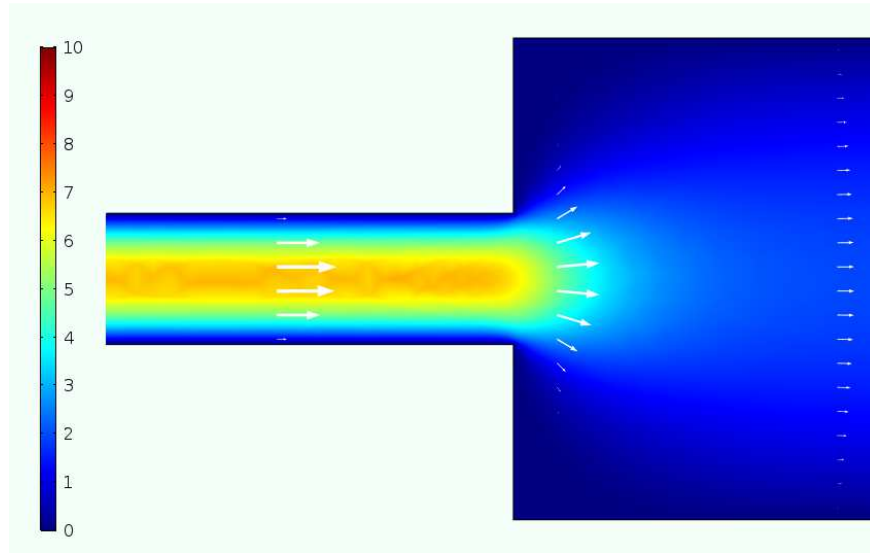


Figure 6. 9. Gas velocity distribution at the inlet point. The velocity scale bar units are m/s.

The velocity of gas increase, as soon as it leaving the cold zone and enter the isothermal zone, due to the increase in its kinetic energy with temperature²⁸⁰, Figure 6.10. The arrows length in Figure 6.10 is proportional to gas velocity, with the maximum velocity in the centre of gas stream ~ 8.5 m/s and the minimum near the quartz walls. The gas velocity distribution changes when the gas mixture crosses over the substrate (Figure 6.11) where the velocity increases above the substrate and a stagnant gas zone is created under the substrate.

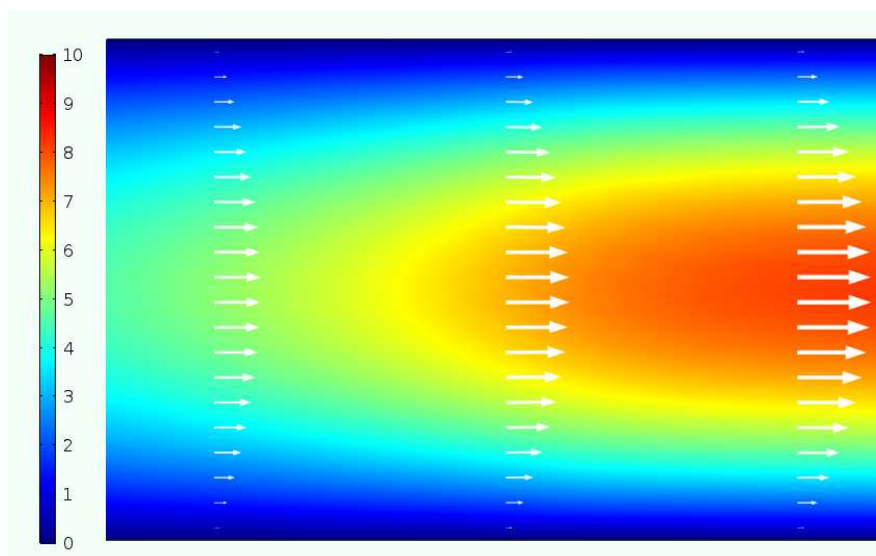


Figure 6. 10. Gas velocity distribution, at the point between the cold and hot zone. The gas velocity increase rapidly when enters the isothermal zone. However, the gas velocity near the reactor wall is ~ 0 m/s. The velocity scale bar units are m/s

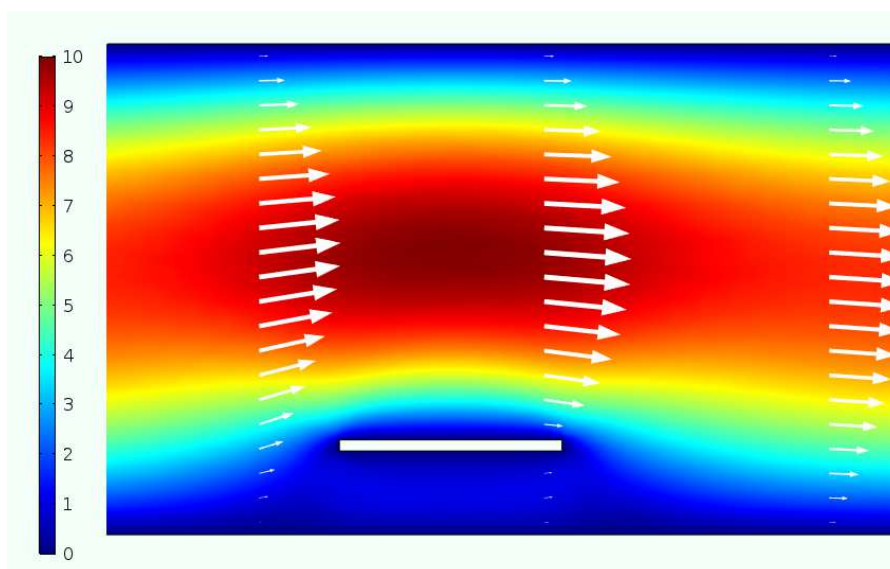


Figure 6. 11. The gas velocity distribution at the middle of the isothermal zone where the sample is located. The gas velocity is at maximum in the centre of gas streamline. The gas in contact with the substrate is steady due to the boundary layer creation. The velocity scale bar units are m/s.

Gas velocity profile along the tube axial length, from inlet down to outlet point, above and below the substrate demonstrate the change in velocity when the gas crosses over the metal substrate (Figure 6.12). Above the sample surface the velocity peaks at ~ 9.8 m/s, while velocity under the sample reaching a maximum velocity of ~ 0.8 m/s. The difference in gas velocity between the top and the bottom faces of the sample creates a

difference in mass delivery between them, *i.e.* the mass flow rate at the top face is higher than the bottom face.

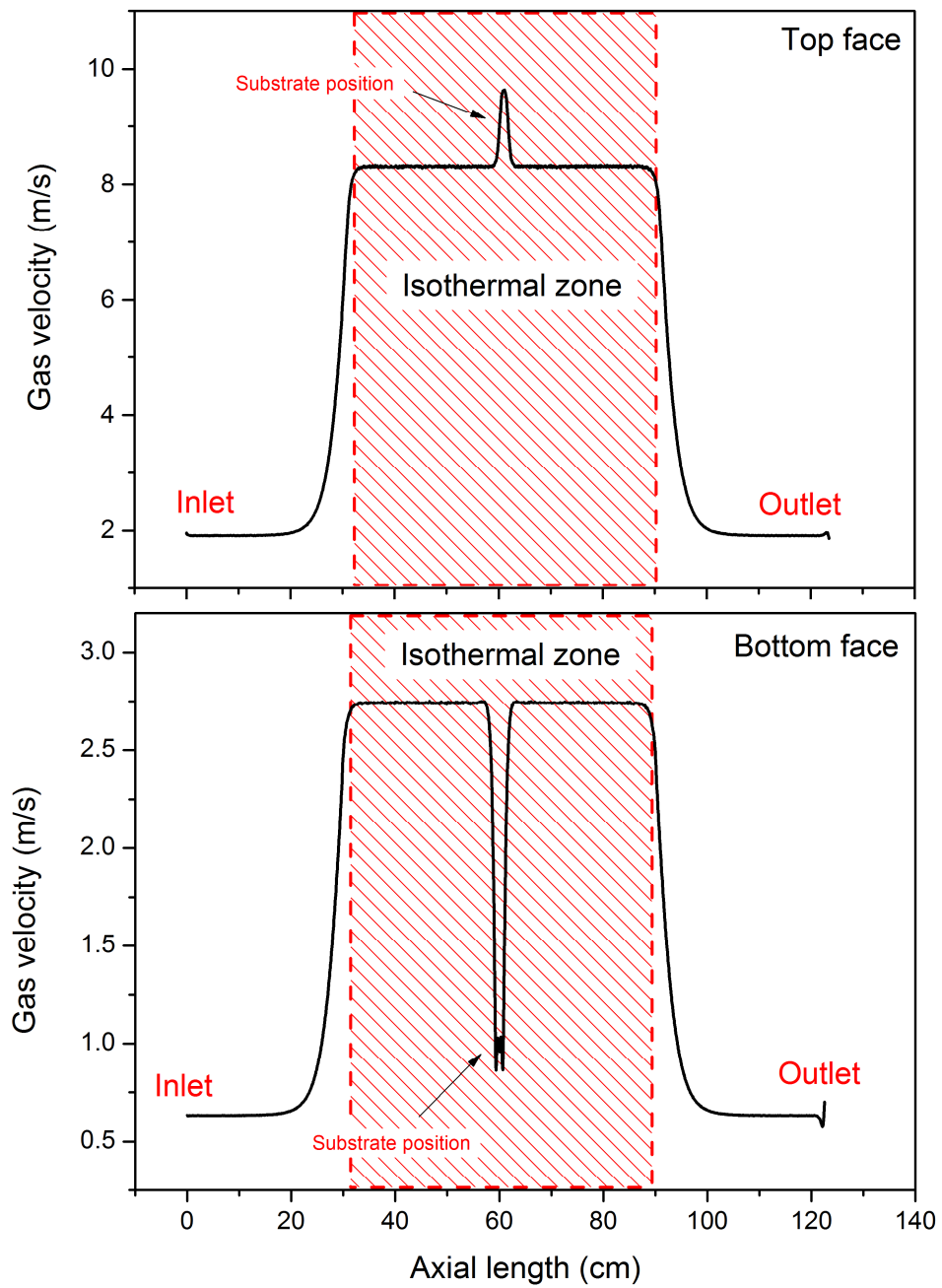


Figure 6. 12. Gas velocity profile from the inlet to the outlet point for different two heights: above the substrate (top face) and beneath the substrate (bottom face). The velocity of gas on the top face of the substrate is higher than the velocity of the gas stream. However, the velocity beneath the sample is very low.

The variation in delivered mass between the substrate top and bottom face results in difference in the growth rate of the graphitic film which is confirmed experimentally in literature²⁸¹ and this work, Figure 6.13.

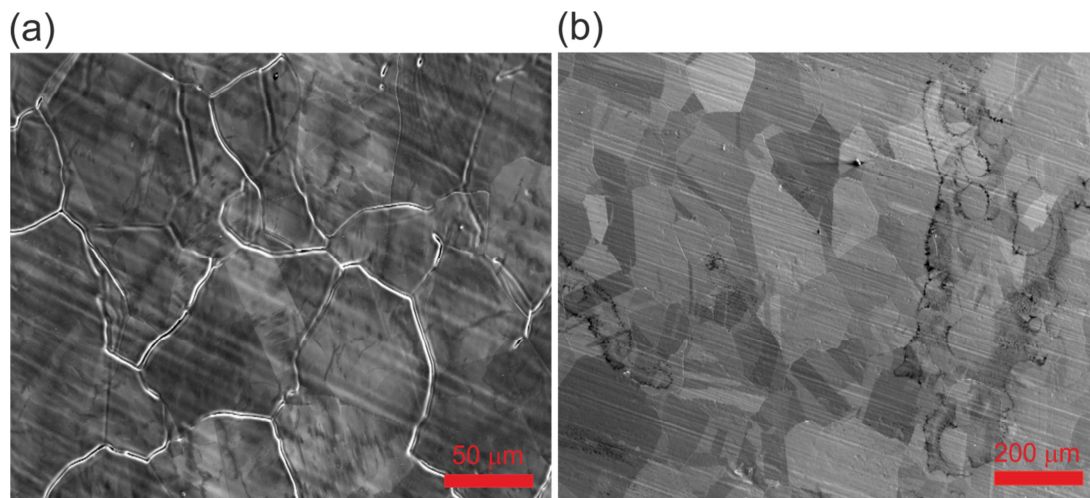


Figure 6. 13. The difference in growth between top and bottom substrate face of Cu33-Ni67. The SEM images clearly show the difference, where graphitic film grows on the top face (a), while the bottom face shows a bar Ni (b). Growth conditions are 1000 °C growth temperature, 0.65 mbar growth pressure, fast cooling rate and growth time 25 min.

The pressure profile of the CVD reactor, Figure 6.14, shows a drop in gas pressure between the inlet and outlet, however, the pressure drop is sharp at the isothermal zone due to change in gas volume.

Based on the fluid flow and heat transfer calculations, the residence time of gas molecules can be estimated from the average gas mixture velocity (~ 8.9 m/s) and found to be 0.067 s. The residence time is an important factor in gas phase kinetics and will be used in the next part calculations.

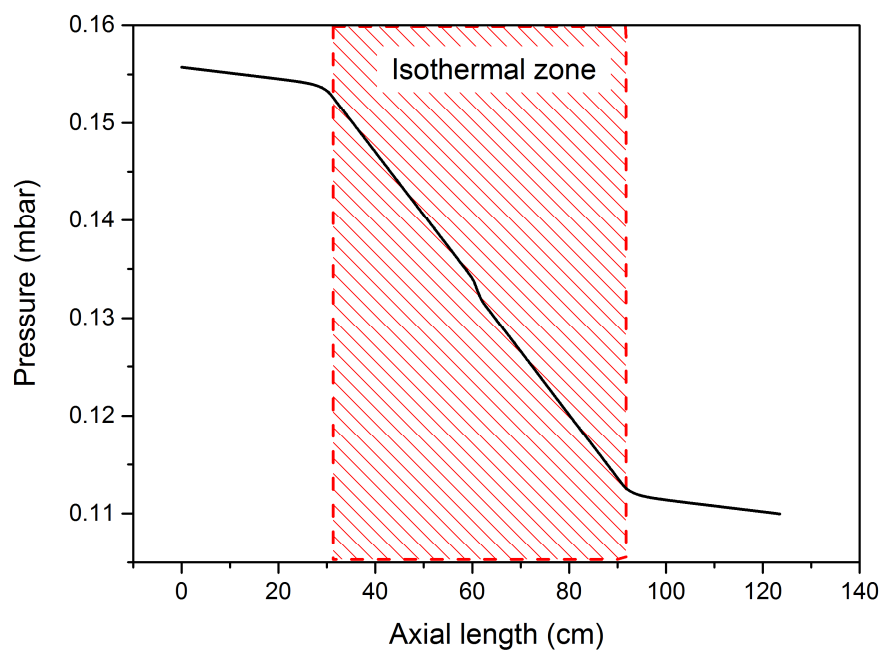


Figure 6. 14. The CVD reactor pressure profile. The pressure difference is clear between the inlets at outlet point. The gas pressure decreases further inside the isothermal zone.

6.4. Gas-Phase Reaction kinetics

CVD system is considered as a plug flow reactor (PFR) or continuous tubular reactor, where chemical reactions continue while the gas mixture is flowing down the axial length of the reactor. Thus, the reactor geometry (length of CVD reactor) directly influences the gas phase kinetics, the longer reactor, the more time to react, *i.e.* longer residence time²⁸².

The gas phase chemical kinetics modelling was performed using the reaction engineering interface provided in COMSOL 5.2a. The advantage of using PFR model is to calculate the chemical species composition at specified residence time (which calculated previously from fluid model). After adding the reaction engineering interface to the model component tree, a reversible reaction group was created that contained 36 chemical reactions and 19 species. The reactions and the species in this study were based on experimental work literature of pyrolysis of CH_4 . The mechanism of pyrolysis of CH_4 is intensively studied, due to the importance of conversion the natural and cheap

CH₄ to more valuable hydrocarbons²⁸³. The reactions were selected based upon Olsvik experimental work at 1000 °C in the presence of H₂^{284–286}. Table 6.2 list all the 36 chemical reactions included in reaction engineering interface model with their activation energy (E), pre-exponential factor (A) and the temperature exponent (n).

Table 6. 2. Elementary chemical reactions used in the model^{284–286}.

Eqn.	Reaction	A (mol/cm ³ .s)	n	E (J/mol)
1	CH ₄ = CH ₃ + H	3.51×10 ¹⁵	0	435344
2	CH ₄ + H = CH ₃ + H ₂	2.25×10 ⁴	3	36703
3	CH ₃ + CH ₃ = C ₂ H ₆	1.01×10 ¹⁵	-0.64	0
4	C ₂ H ₆ + H = C ₂ H ₅ + H ₂	5.54×10 ²	3.5	21658
5	C ₂ H ₆ + CH ₃ = C ₂ H ₅ + CH ₄	0.55	4	34727
6	C ₂ H ₅ = C ₂ H ₄ + H	2.00×10 ¹³	0	166184
7	CH ₃ + CH ₃ = C ₂ H ₄ + H ₂	1.00×10 ¹⁶	0	133952
8	C ₂ H ₄ + CH ₃ = C ₂ H ₃ + CH ₄	6.62	3.7	39817
9	C ₂ H ₄ + CH ₃ = C ₃ H ₇	3.31×10 ¹¹	0	32295
10	C ₂ H ₄ + H = C ₂ H ₃ + H ₂	1.32×10 ⁶	2.53	51312
11	C ₂ H ₃ = C ₂ H ₂ + H	1.93×10 ²⁸	-4.783	214001
12	CH ₃ + C ₂ H ₃ = C ₃ H ₆	1.00×10 ¹³	0	0
13	C ₃ H ₇ = C ₃ H ₆ + H	1.58×10 ¹⁶	0	159068
14	C ₃ H ₆ = C ₃ H ₅ + H	1.00×10 ¹⁵	0	368368
15	C ₃ H ₅ = C ₂ H ₂ + CH ₃	3.16×10 ¹⁰	0	151533
16	C ₃ H ₅ = C ₃ H ₄ + H	5.00×10 ⁹	0	146510
17	C ₃ H ₅ + H = C ₃ H ₄ + H ₂	1.00×10 ¹³	0	0
18	C ₃ H ₆ + H = C ₃ H ₅ + H ₂	3.16×10 ¹¹	0	18837
19	C ₂ H ₃ + C ₂ H ₃ = C ₄ H ₆	1.26×10 ¹³	0	0
20	C ₂ H ₃ + C ₂ H ₄ = C ₄ H ₆ + H	5.00×10 ¹¹	0	30621
21	C ₂ H ₂ + H = C ₂ H + H ₂	6.02×10 ¹³	0	93348
22	C ₂ H ₂ + CH ₃ = C ₂ H + CH ₄	1.81×10 ¹¹	0	72418
23	C ₄ H ₆ + H = C ₄ H ₅ + H ₂	1.00×10 ¹⁴	0	62790
24	C ₄ H ₅ = C ₄ H ₄ + H	1.00×10 ¹⁴	0	173300

25	$C_2H + H = C_2H_2$	1.81×10^{14}	0	0
26	$C_2H_3 + C_2H_2 = C_4H_5$	1.10×10^{12}	0	16744
27	$CH_3 + CH_3 = C_2H_5 + H$	1.80×10^{12}	0	43534
28	$C_4H_5 + C_2H_2 = C_6H_6 + H$	6.02×10^{12}	0	37674
29	$C_2H_4 = C_2H_3 + H$	1.00×10^{16}	0	452088
30	$C_2H_5 + C_2H_2 = C_2H_6 + C_2H$	2.71×10^{11}	0	97952
31	$C_2H_5 + H = C_2H_6$	3.07×10^{13}	0	0
32	$C_2H_4 = C_2H_2 + H_2$	7.94×10^{12}	0.44	371549
33	$C_2H_3 + H = C_2H_2 + H_2$	9.64×10^{13}	0	0
34	$C_2H_2 + CH_3 = C_3H_4 + H$	6.20×10^{11}	0	83720
35	$C_3H_6 = C_3H_4 + H_2$	8.00×10^{12}	0.44	339694
36	$C_3H_6 + CH_3 = C_3H_5 + CH_4$	1.58×10^{12}	0	36837
Chemical species: CH ₄ , CH ₃ , H, H ₂ , C ₂ H ₆ , C ₂ H ₅ , C ₂ H ₄ , C ₂ H ₃ , C ₂ H ₂ , C ₂ H, C ₃ H ₇ , C ₃ H ₆ , C ₃ H ₅ , C ₃ H ₄ , C ₄ H ₆ , C ₄ H ₅ , C ₄ H ₄ , C ₆ H ₆ .				

The chemical reaction rates calculated in COMSOL are based upon a modified Arrhenius equation²⁸⁷:

$$k = A.T^n \exp\left(-\frac{E}{RT}\right) \quad 6.12$$

where A denotes the pre-exponential factor (mol/cm³.s), T is the temperature in Kelvin, n the temperature exponent, E the activation energy (J/mol) and R the gas constant (J/(mol.K)). The reactor pressure and temperature were set according to the experimental conditions of this work and the residence time value extracted from heat tranfer and fluid flow meodel. The percentage of CH₄ conversion and the yield of chemical species were calculated from the following equations²⁸⁸:

$$X_{CH_4} = \frac{n_{CH_4.converted}}{n_{CH_4.feed}} \times 100\% \quad 6.13$$

$$Y_{H_2} = \frac{n_{H_2}}{2 \times n_{CH_4.feed}} \times 100\% \quad 6.14$$

$$Y_{C_xH_y} = \frac{x \times n_{C_xH_y}}{n_{CH_4, feed}} \times 100\% \quad 6.15$$

6.4.1. Results

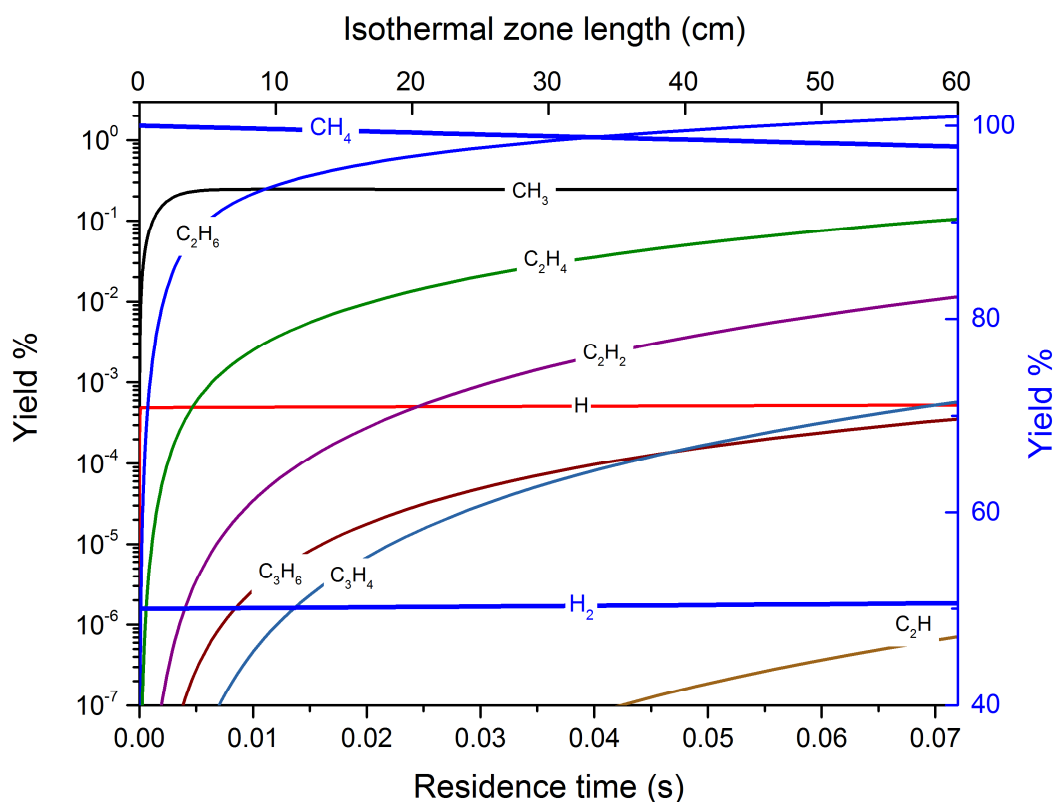


Figure 6. 15. Chemical species yield versus residence time for CH_4 and H_2 mixture a 2:1 by volume mixing ratio at 1000 °C and 0.1 mbar pressure. The top x-axis scale is the correspondence isothermal distance. The blue y-axis is the CH_4 and H_2 yield.

Figure 6.15 shows the species yield as a function of the residence time for the products and intermediates. It is obvious that the conversion of CH_4 increases with increasing residence time and hence is accompanied by an increase in the species yield. The correspondence length scale is shown at the top x-axis, which suggests that chemical species yield for all species are higher near the outlet of the isothermal zone than the inlet. The highest yield species resulting from CH_4 decomposition are C_2H_6 , C_2H_4 and

C_2H_2 (Figure 6.16), which is confirmed by experimental and theoretical work in the literature^{285,286,288–295}

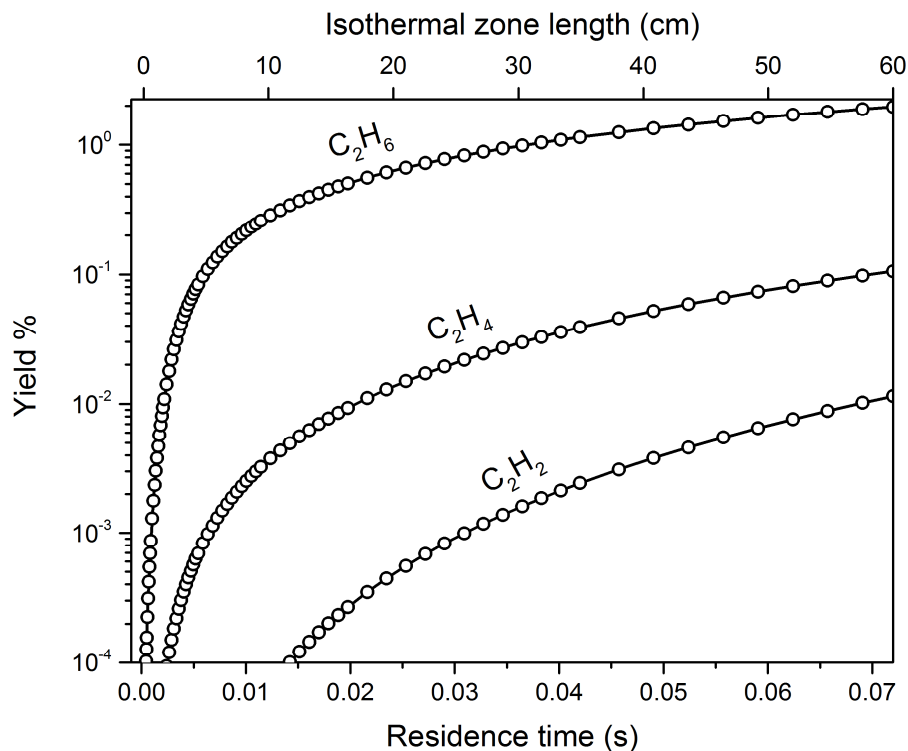
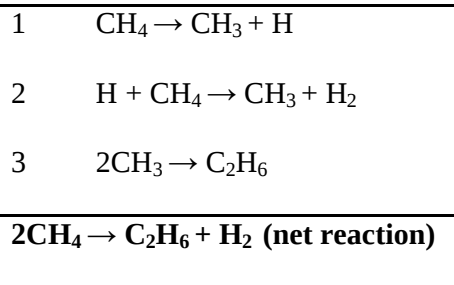


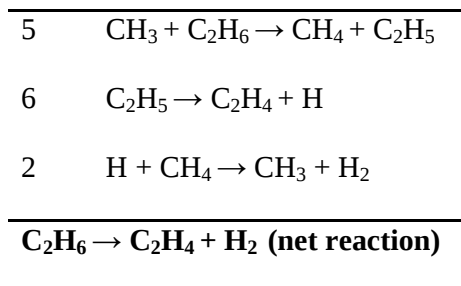
Figure 6. 16. The yield of the three main species versus residence time, C_2H_6 shows higher yield than C_2H_4 and C_2H_2 . The yield profile of the three hydrocarbons keeps increasing down the reactor.

According to Back²⁹², the primary decomposition reaction of CH_4 results in C_2H_6 and H_2 which presented by chemical equations:

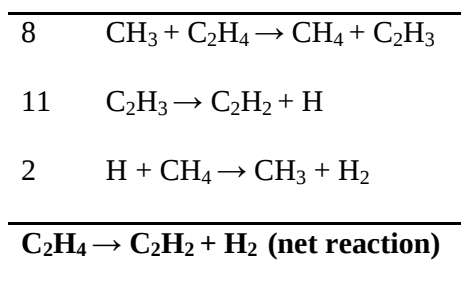


At the initial stage reaction, reaction 1 is the only source for CH₃ radical, and it is the rate controlling reaction.

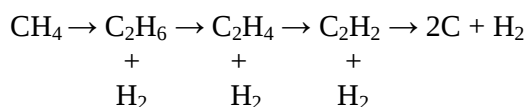
C₂H₄ is a product of C₂H₆ secondary reactions:



C₂H₂ production possibly follows the mechanism:



Therefore, the production of the three primary hydrocarbons is due to the stepwise dehydrogenation with the aid of H₂²⁸⁴:



After a very short time, the only products are C₂H₆ and H₂, which then further decomposes to produce C₂H₄. If the residence time is long enough, the C₂H₂ yield dominate and become the main product. So for the CVD system under study conditions, C₂H₆ is the main product because its yield is high and increases down the CVD reactor

(~ 1.96 %). The C_2H_4 and C_2H_2 yield increase when the residence time is increased (Figure 6.17).

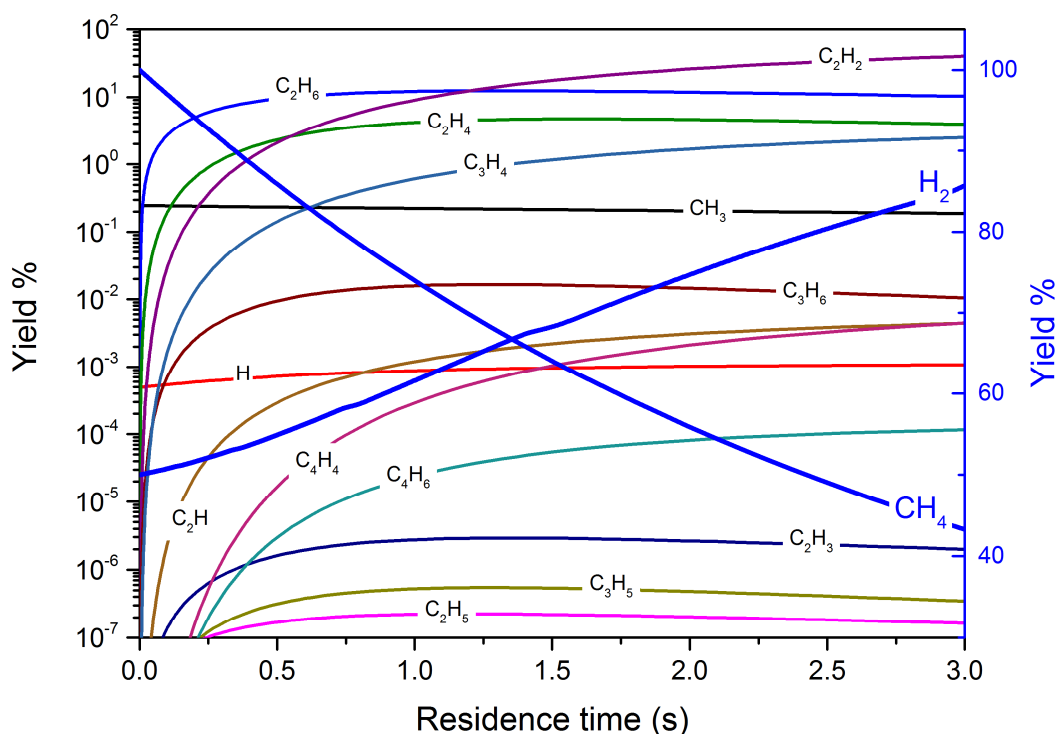


Figure 6. 17. Chemical species yield versus residence time of CH_4 and H_2 mixture 2:1 by volume mixing ratio at 1000 °C and 0.1 mbar pressure. The conversion of CH_4 increase with increasing residence time and C_2H_2 shows the highest yield after 3 seconds. The blue y-axis is the CH_4 and H_2 yield.

The C_2H_2 yield reaches 39.96 % near the isothermal zone outlet at 3 s residence time, this long residence time is reported for atmospheric pressure growth for the same CVD system²⁸¹. The thermal decomposition of CH_4 is strongly dependent on residence time and temperature, increasing temperature above 1200 °C with a short time 10^{-2} s results in the production of C_2 hydrocarbons²⁹⁶. Figure 6.18 showing the product yield as a function of temperature at 0.072 s residence time. At 1200 °C the model shows that almost all of the CH_4 is converted to other products, mainly H_2 and C_2H_2 , C_2H_6 , C_2H_4 and C_3H_4 .

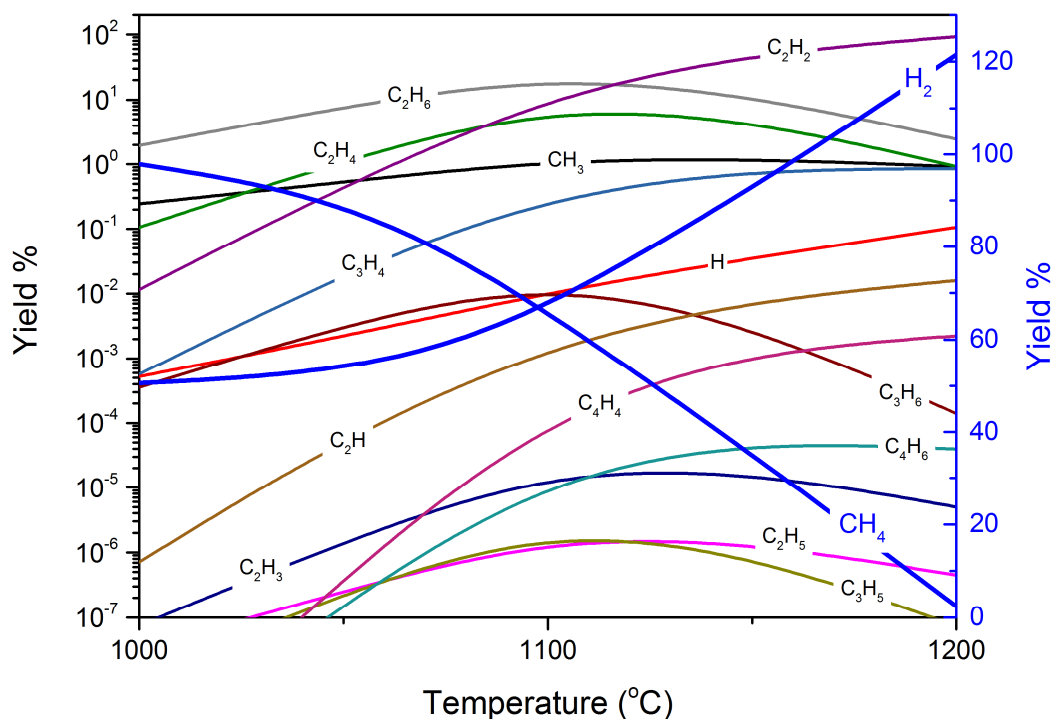


Figure 6.18. The yield of chemical species at 0.072 s residence time of CH₄ and H₂ mixture 2:1 by volume mixing ratio at temperature 1000 - 1200 °C and 0.1 mbar pressure.

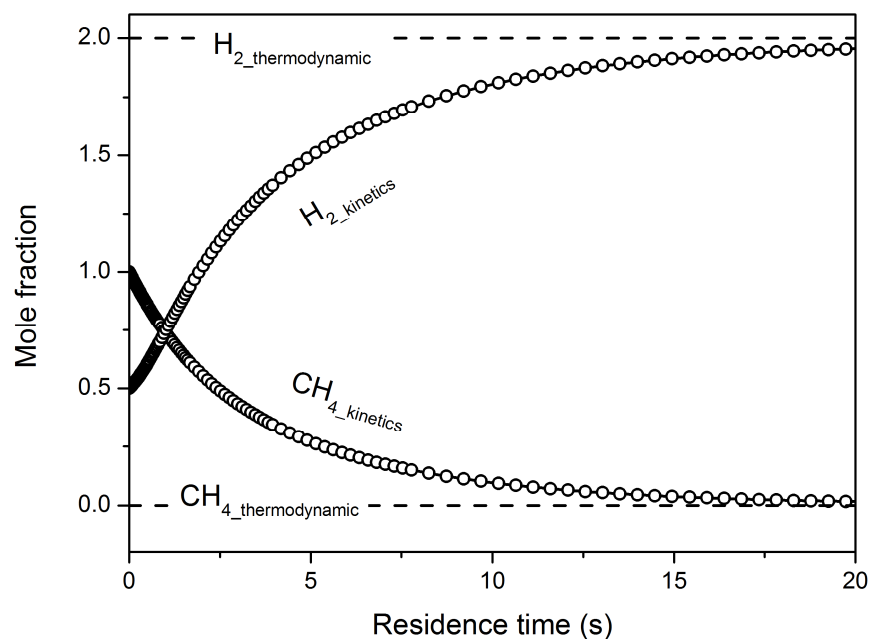


Figure 6.19. CH₄ and H₂ mixture 2:1 by volume versus residence time. The two gases required 3 seconds at 1000 °C and 0.1 mbar to reach their thermodynamic equilibrium values. Both CH₄ and H₂ thermodynamic values taken from figure 6.10.

Comparing the thermodynamics calculation with the kinetics model, it seems that CH₄ and H₂ reach the thermodynamics mole fraction value under the same experimental

conditions (pressure and temperature) after 20 s (Figure 6.19) which is longer than the calculated residence time for low-pressure CVD but is possibly achieved at atmospheric pressure.

It can be concluded from the results of gas phase kinetics model, that CH_4 thermal decomposition occurs continuously down the isothermal zone of the reactor and not all of the CH_4 feedstock is converted due to short reaction time. Subsequently, this results in concentration difference in the CH_4 decomposition products within the CVD isothermal chamber. The difference in concentration of active species leads to variation in growth rate with respect to the substrate position inside the CVD chamber which is experimentally confirmed. Li et al. show that there is a difference in graphene film thickness grows by CVD at different substrate position. SLG film grows in a position near the gas inlet while the thickness is increased to FLG near the gas outlet²⁹⁷.

According to gas phase model, thermodynamic equilibrium is not achieved at low pressure, which is attributed to short gas residence time (0.072 s); it requires ~ 3 s to achieve equilibrium which is possible in some atmospheric pressure CVD reactors.

Therefore, the gas phase reaction in CVD is kinetically controlled and depends highly on the residence time that is determined by experimental conditions²⁹⁸.

6.5. Chemical surface reactions

The reaction of CH_4 with transition metals is believed to be a stepwise reaction as proposed by Grabke et al.²⁹⁹. The dissociation of chemisorbed CH_4 on Ni confirmed using molecular beam study, which stated that when CH_4 molecule approaches Ni surface loses one of its H due to the molecule deformation³⁰⁰. CVD growth of graphene

is a surface reaction process ¹¹¹ where CH₄ decompose on the substrate surface in a stepwise manner giving C in the final stage as described in Table 6.3.

In this section, a simple surface reaction model is presented, and the results are compared with the experimental findings. The model based on the following assumptions:

- I. The only C source is the dehydrogenation of CH₄ because its concentration is higher than the other hydrocarbon in the gas phase (according to gas-phase reaction model). Furthermore, the surface reaction mechanism of other species, like C₂H₂, not fully known ³⁰¹.
- II. The rate limiting step is assumed R6, as suggested by Fan et al. ³⁰² due to its high energy barrier.
- III. Steps R1-R5 assumed in quasi-equilibrium.
- IV. The graphene growth on the surface happens only when C in the bulk reach threshold concentration (saturation) which assumed to be solubility concentration ²⁰².
- V. According to assumption IV, the life time of surface C is very short due to the diffusion, therefore C coverage (Θ_C) can be safely neglected, *i.e.* it can be assumed that all the surface C diffuse to the bulk at a very fast rate which is confirmed by experimental observations and literature ³⁰³.

Therefore, the model aims to estimate the time required to reach the C solubility limit for a given substrate thickness, *i.e.* $C_{surface} = C_{saturation} = C_{solubility}$.

Table 6. 3. Proposed surface reactions mechanism with the rate equations.

Reaction	Chemical equation	Rate
R1	$CH_{4(g)} + S \leftrightarrow CH_{4(s)}$	$k_1 P_{CH4} \theta_s - k_1^{-1} \theta_{CH4}$
R2	$H_{2(g)} + 2S \leftrightarrow 2H_{(s)}$	$k_2 P_{H2} \theta_s - k_2^{-1} \theta_H \theta_H$
R3	$CH_{4(s)} + S \leftrightarrow CH_{3(s)} + H_{(s)}$	$k_3 \theta_{CH4} \theta_s - k_3^{-1} \theta_{CH3} \theta_H$
R4	$CH_{3(s)} + S \leftrightarrow CH_{2(s)} + H_{(s)}$	$k_4 \theta_{CH3} \theta_s - k_4^{-1} \theta_{CH2} \theta_H$
R5	$CH_{2(s)} + S \leftrightarrow CH_{(s)} + H_{(s)}$	$k_5 \theta_{CH2} \theta_s - k_5^{-1} \theta_{CH} \theta_H$
R6	$CH_{(s)} + S \leftrightarrow C_{(s)} + H_{(s)}$	$k_6 \theta_{CH} \theta_s - k_6^{-1} \theta_C \theta_H$
R7	$C_{(s)} \rightarrow C_{(Bulk)}$	$-D \left(\frac{C_{(s)} - C_{(Bulk)}}{t_{substrate}} \right)$

D: diffusion coefficient (cm²/s), (g): gas phase, (s): surface , t: substrate thickness in cm.

The following equations express the surface coverage fraction (Θ) for the species CH₄, H, CH₃, CH₂ and CH:

$$\theta_{CH4} = K_1 P_{CH4} \theta_s \quad 6.16$$

$$\theta_H = \sqrt{P_{H2} K_2} \theta_s \quad 6.17$$

$$\theta_{CH3} = \frac{K_3 P_{CH4} \theta_s}{\theta_H} \quad 6.18$$

$$\theta_{CH2} = \frac{K_4 P_{CH3} \theta_s}{\theta_H} \quad 6.19$$

$$\theta_{CH} = \frac{K_5 P_{CH2} \theta_s}{\theta_H} \quad 6.20$$

substituting each value with its correspondence yield:

$$\theta_{CH3} = \frac{K_1 K_3 P_{CH4} \theta_S}{\sqrt{P_{H2} K_2}} \quad 6.21$$

$$\theta_{CH2} = \frac{K_1 K_3 K_4 P_{CH4} \theta_S}{P_{H2} K_2} \quad 6.22$$

$$\theta_{CH} = \frac{K_1 K_3 K_4 K_5 P_{CH4} \theta_S}{(P_{H2} K_2)^{3/2}} \quad 6.23$$

substituting equations (6.21)-(6.23) in the rate-limiting step (R6) gives:

$$r = k_6 \left[\frac{K_1 K_3 K_4 K_5 P_{CH4} \theta_S^2}{(K_2 P_{H2})^{3/2}} - \frac{\theta_C \theta_S (K_2 P_{H2})^{1/2}}{K_6} \right] \quad 6.24$$

where K_1 - K_6 is equilibrium constant which is expressed as:

$$K = \frac{k_{forward}}{k_{reverse}} \quad 6.25$$

k is the reaction rate calculated using the following Arrhenius equation

$$k = A \exp\left(-\frac{E}{RT}\right) \quad 6.26$$

A is a pre-exponential factor, E activation energy in (J/mol) and R gas constant, 8.3144 (J/K.mol).

θ_S is a fraction of free (unblocked) surface sites, assuming all the species take part in surface coverage, the summation of all fractions equal to 1:

$$1 = \theta_{CH4} + \theta_{CH3} + \theta_{CH2} + \theta_{CH} + \theta_H + \theta_S \quad 6.27$$

substituting equations (6.16), (6.17) and (6.21)-(6.23) in (6.27) and solve for θ_S :

$$\theta_S = \frac{1}{1 + K_1 P_{CH4} + \sqrt{P_{H2} K_2} + \frac{K_1 K_3 P_{CH4}}{\sqrt{P_{H2} K_2}} + \frac{K_1 K_3 K_4 P_{CH4}}{P_{H2} K_2} + \frac{K_1 K_3 K_4 K_5 P_{CH4}}{(P_{H2} K_2)^{3/2}}} \quad 6.28$$

The activation energy values for the reactions R1-R6 are tabulated in Table 6.4, the pre-exponential factors values of surface reactions are assumed 1×10^{13} (s^{-1}) which is generally used when the experimental value is not known^{304,305}. While the pre-

exponential factors for molecular adsorption (reaction R1 and R2) are set 1000 ($\text{Pa}^{-1} \cdot \text{s}^{-1}$)³⁰⁵ and for dissociative adsorption of H_2 on Ni set to 0.01 based on experimental work²¹⁹.

Table 6. 4. List of forwarding and reverse activation energies ($\text{kJ} \cdot \text{mol}^{-1}$), for surface reactions model.

Reaction	Cu		Ni		Cu90-Ni10		Cu50-Ni50	
	E_f	E_r	E_f	E_r	E_f	E_r	E_f	E_r
R1	0	1.9297 ^{306,307}	0	1.9297 ³⁰⁷	0	1.9297 ³⁰⁷	0	1929.7 ³⁰⁷
R2	29 ³⁰⁸	62.8 ³⁰⁸	0	92 ¹⁵⁶ (95 ⁽³⁰⁹⁾)	same values as Ni according to ref.312			
R3	126.4 ³¹⁰	86.841 ³¹⁰	87.802 ³¹¹	86.84 ³¹¹	100.34 ³¹⁰	74.289 ³¹⁰	127.36 ³¹²	120.606 ³¹²
R4	121.57 ³¹⁰	51.136 ³¹⁰	67.54 ³¹¹	60.786 ³¹¹	89.731 ³¹⁰	38.594 ³¹⁰	74.294 ³¹²	43.419 ³¹²
R5	89.731 ²⁸³	38.594 ²⁸³	33.77 ²⁸⁴	66.575 ²⁸⁴	63.68 ²⁸³	29.91 ²⁸³	44.383 ²⁸⁵	44.383 ²⁸⁵
R6	190.08 ²⁸³	38.6 ²⁸³	128.33 ²⁸⁴	78.153 ²⁸⁴	148.59 ²⁸³	34.74 ²⁸³	157.27 ²⁸⁵	71.398 ²⁸⁵

6.5.1. Results

Figure 6.20 show that for Ni, it takes 216 min to reach the C solubility value, which is in excellent agreement with the experimental observation (210 min). Moreover, the model agrees well in terms of time required with respect to Ni substrate thickness. However, the model does not match the exponential decay of the growth time with respect to gas pressure when Ni substrate is used (Figure 6.21). The model predicts an exponential behaviour at different growth pressure but the predicted incubation time three times higher than the experimental observations and the divergence increase when the growth pressure increase. This might be attributed to the fact that the model is working only on CH_4 as a C source, however, according to thermodynamic and kinetic calculations (Figures 6.1 and 6.15 respectively), by increasing growth pressure the concentration of other species other than CH_4 significantly increase.

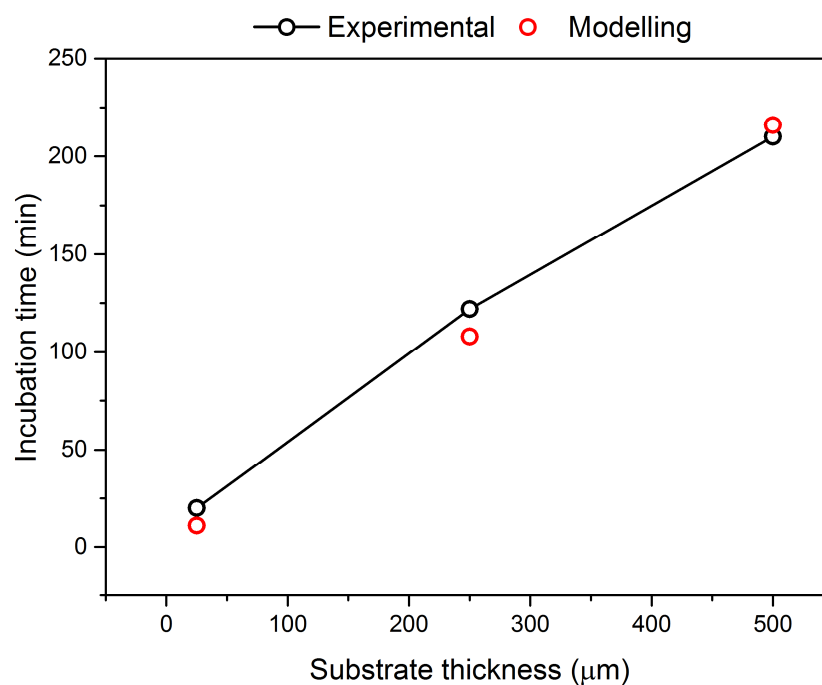


Figure 6. 20. Surface reaction model prediction of the incubation time of three different Ni foil thickness in comparison with experimental results. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure, 5.2 and 2.6 sccm flow rate of CH_4 and H_2 respectively and fast cooling rate.

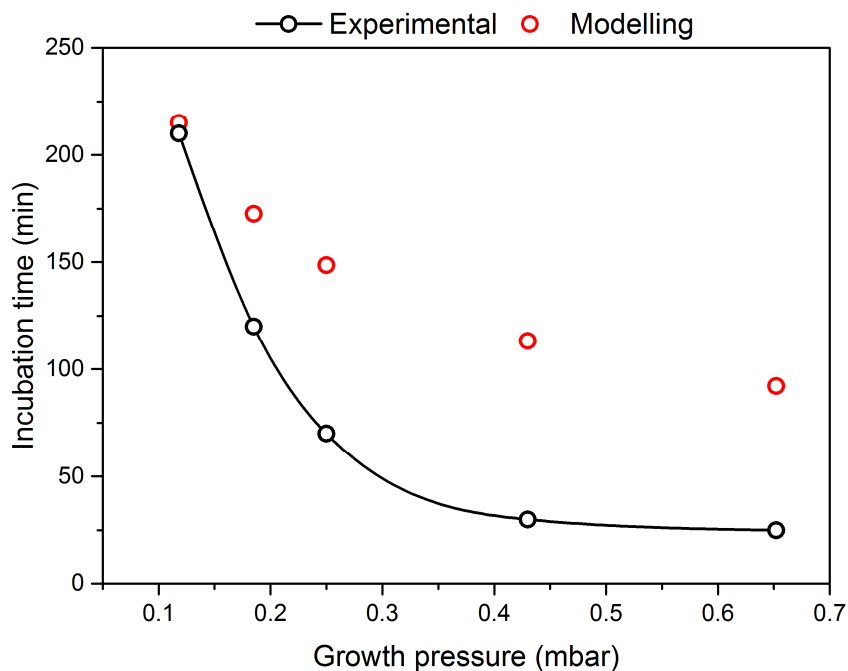


Figure 6. 21. Surface reaction model prediction of the incubation time of 500 μm Ni foil thickness at different growth pressure in comparison with experimental results. Growth conditions are 1000 °C growth temperature, 2:1 by volume flow rate of CH_4 and H_2 respectively and fast cooling rate.

Therefore, at high-pressure reaction rate need to be adjusted by including C coming from other species such as C_2H_2 , C_2H_6 and C_2H_4 which their catalytic decomposition reaction not proposed so far.

Figure 6.22 shows the model prediction for the substrates listed in Table 6.4 together with the experimental results from this study, the incubation time prediction agrees well with the actual time required experimentally for this work.

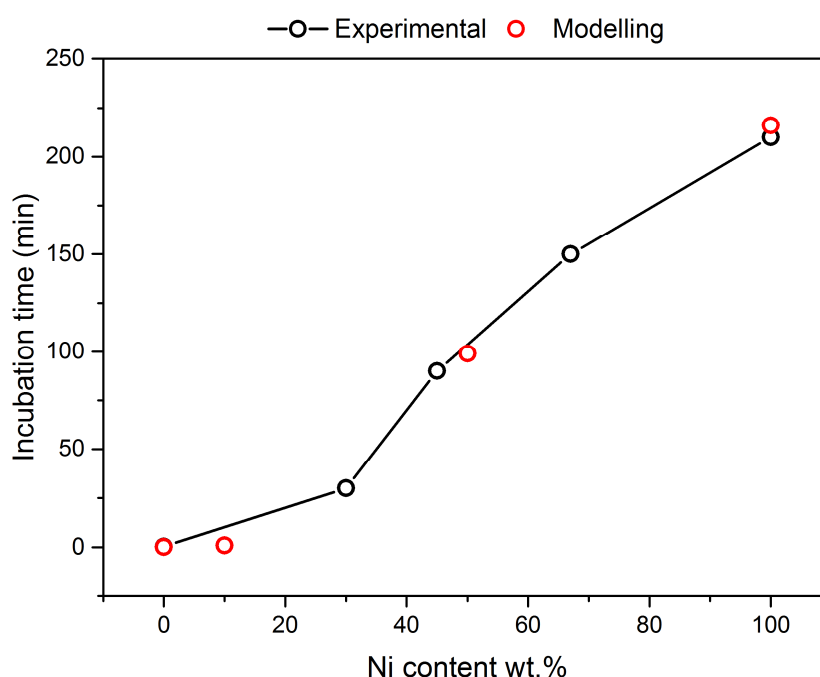


Figure 6. 22. Model and experimental results of CVD graphene on Cu-Ni alloy. Growth conditions are 1000 °C growth temperature, 0.1 mbar growth pressure, 5.2 and 2.6 sccm flow rate of CH_4 and H_2 respectively and fast cooling rate.

6.6. Conclusion

The CVD growth process of graphene on a Cu-Ni alloy was investigated theoretically from both a thermodynamic and kinetic perspective. For the thermodynamic viewpoint, two cases were considered; the thermodynamics in the gas phase with no solid C being present and the thermodynamics with solid C included. In the gas phase, two regions have been recognised, below 800 °C and above 800 °C. The first region shows the

constant concentration of C_6H_6 and C_2H_4 , with no growth shown on Cu-Ni surface. The C_6H_6 and C_2H_4 concentration start to decline at a temperature $> 800\text{ }^{\circ}\text{C}$ which is the start of the second region in which C_2H_2 and C_4H_2 are dominated, and graphene grows on Cu. The estimation of the deposition driving force from thermodynamic equilibrium showed that the maximum value of driving force was reached at $> 800\text{ }^{\circ}\text{C}$, explaining why growth is only experimentally observed to start at this temperature under these conditions¹¹⁶.

The gas phase kinetics simulation showed that the CH_4 conversion was $\sim 2.15\%$ and the active species concentration increase downstream. C_2H_6 , C_2H_4 and C_2H_2 are the main CH_4 decomposition species and their concentration increase with residence time, which rise as an important factor in CVD growth.

The microkinetics of reactions on Cu-Ni surfaces shows a good agreement with the experimental results. However, the model fails to mimic the experimental findings at different growth pressure. At high pressure, the concentration of the hydrocarbons produce from CH_4 cannot be ignored and essentially need to be taken into account in microkinetics of surface reactions. Unfortunately, the microkinetics surface mechanisms of the C_2 hydrocarbons are not fully known until today.

7. Conclusion

In this thesis, the role of C solubility on the growth of CVD graphene has been investigated using a range of growth substrates with different carbon affinities. The CVD growth of graphene was first performed on pure Ni and Cu, and then merged in Cu-Ni alloys where all the substrates have a 500 μm thickness. The alloys comprised 0, 30, 45, 67 and 100 wt. % Ni with a balance of Cu which gave Cu-Ni substrates of C solubility values of 0.004, 0.03, 0.1, 0.158 and 0.183 wt. % respectively. The deposition of the graphene was performed in a hot-wall reactor under growth conditions: 0.1 mbar pressure, 1000 $^{\circ}\text{C}$ temperature and a feedstock of CH_4 : H_2 2:1 by volume. The deposited films are characterised in situ on the growth substrate by Raman spectroscopy and SEM.

The results of CVD graphene on pure Cu showed a coverage of 16% and 74% SLG and BLG respectively over the 500 μm Cu thick, but 98% SLG coverage over the 25mm, under the same growth conditions. The study was extended to include 250 and 1000 μm Cu thick substrates and showed a correlation between the Cu thickness and graphene coverage. The SLG coverage decreased, and the BLG coverage increased with increasing Cu substrate thickness. The possible explanation is that increasing Cu thickness allows more C to dissolve in the bulk, which might then diffuse back to the surface upon cooling. Expanding the growth parameters space shows that no graphene grows at temperature below 900 $^{\circ}\text{C}$ at 0.1 mbar pressure on the 500 μm Cu thick, which is confirmed by Raman spectroscopy and SEM results. However, by increasing growth pressure to 0.65 mbar, defective graphene grows at 800 $^{\circ}\text{C}$.

On the other hand, pure Ni promoted graphitic growth with long incubation period (210 min), due to high C solubility in Ni. Furthermore, by decreasing the Ni thickness down

to 25 μm , the growth time reduced to 30 mins and linear relationship were found between the incubation time and Ni thickness. Moreover, growth at different pressures was found to exponentially reduce the incubation time, which could be attributed to increasing the number of adsorbed methane molecules on the Ni surface.

Chapter 5 showed the results of the CVD graphene grown on Cu-Ni substrates. The deposited graphitic films were mainly FLG at standard growth conditions, while by increasing growth pressure to 0.65 mbar, graphene coverage improved to BLG. It is found that the CVD graphene quality is sensitive to the Ni content in the Cu-Ni matrix; the SLG and BLG coverage decreases while the FLG coverage increases with a higher Ni content in the catalyst substrate. Also it is found that the trend of incubation time and C solubility is the same with respect to Ni content in the Cu-Ni system, *i.e.* the incubation time and C solubility increase with increasing Ni content in the Cu-Ni substrate. In addition, the incubation time is reduced with increasing growth pressure; however, the incubation time and C solubility behaviour with Ni content did not changed.

Cooling rates of the Cu-Ni samples after growth is another area investigated; it was found that the substrate surface coverage has a transition point with respect to Ni content in the alloy. The surface coverage of the Cu-rich substrate was found to be $> 90\%$ when it cools down at a fast rate ($376\text{ }^{\circ}\text{C}/\text{min}$), while the surface coverage reduced to $< 20\%$ at slow cooling rates ($27\text{ }^{\circ}\text{C}/\text{min}$). However, the Ni-rich substrates showed the reverse behaviour. Involving GDOES to depth profile the carbon content as a function of depth in the substrate found that at a fast cooling rate all the substrates have constant bulk composition. However, at a slow cooling rate, the Cu-rich substrates show a subsurface composition inhomogeneity represented by increasing Ni, while this behaviour is not observed in Ni-rich substrates. The inhomogeneity in the subsurface

composition results in C solubility variation within the same substrate, which could establish a diffusion barrier against C precipitation to the surface. The GDOES also revealed that the bulk C concentration is higher for the fast cooling rates than for the slow cooling samples. This result supports the proposed diffusion–segregation mechanism of CVD graphene on Cu-Ni substrate.

CVD is a complex process because of the contribution of many parameters, such as growth temperature and pressure which play an important role in the thermodynamic of the CVD process. Other parameters, such as CVD chamber geometry, gas residence time, gas flow rate, substrate material and thickness, substrate surface area and carbon solubility are mainly the kinetic controlling parameters. Therefore the final chapter showed the results of modelling the CVD process for both thermodynamic and kinetics parameters. The gas phase thermodynamic modelling for the experimental growth conditions (1000 °C, 0.1 mabr and CH₄: H₂ 2:1 by volume) showed that the difference in C chemical potential between the gas phase and above the substrate reaches its maximum at 900 °C ,which is considered the driving force of deposition. Moreover, the thermodynamic modelling also revealed the role of oxygen in the CVD growth of graphene beside C and H. The experimental data from literature was scattered on the C-H-O phase diagram to map the graphene growth boundaries. It was found that the growth boundaries ratios of H and O were $X_H = 0.9996$ and $X_O = 0.4$ respectively, where no growth was recorded below these values. The highest published C ratio was found to be $X_C = 0.666$.

Modelling the kinetic part included a fluid and heat transfer models. The kinetic model revealed that the velocity of reactant gas on the top face of the sample was higher than the bottom face, which results in a difference in film coverage between the two faces. No growth observed on the bottom surface while the top was fully covered. The kinetics

of gas phase was also investigated, and it was found that thermodynamic equilibrium cannot be reached under growth conditions for this study, due to the short residence time. However, thermodynamic equilibrium would be achieved with longer residence times, which might be at atmospheric pressure. The non-thermodynamic equilibrium of the gas-phase leads to a variation in the concentration of active species inside the CVD reactor which increases down the reactor axial length. The differential concentration of the growth active species leads to a differential in the growth rate which is experimentally approved.

The final part of the modelling is the surface reaction based on the assumption of CH_4 dehydrogenation, which showed good agreement between the model and the experimental results in terms of the incubation time. However, the model did not match the experimental findings at high growth pressure which might be because other active species take part in the growth process which need to be considered in future work.

8. Further Work

The Cu-Ni alloys system adopted in this work successfully demonstrate the impact of C solubility on the CVD graphene growth. The CVD of graphene field would benefit from the deeper understanding of the role of C solubility in the catalytic substrate on the growth mechanism, which could be consider for better substrate selection. Also, this study provides a tool to control the graphene number of layers by controlling the solubility of C and the thickness of the substrate. The comprehensive model (thermodynamic and kinetics) presented in this study could be applied to other CVD systems to aid synthesis of graphene coating for requested applications.

Further work is still required to investigate in more detail the effect of Cu thickness on CVD graphene. In this work, the Cu thicknesses used are 25, 250, 500, and 1000 μm ; the range could be extended to include more thicknesses, such as 100 and 300 μm , to fill the gap between the 25 μm and 250 μm and build a full understanding of the influence of thickness on CVD graphene. Furthermore, contributing more thicknesses in the study would highlight the impact of Cu thickness on the graphitic film thickness, which might be a new way to control the number of graphene layers.

The three Cu-Ni alloys used in this work showed the influence of C solubility on the mechanism of CVD graphene; however, involving more Cu-Ni concentration would add more details to the study. Another factor needs to be investigated, the Cu-Ni substrate thickness, because the dissolved C is directly proportional to the thickness of the substrate. Therefore, it would be a good way to control the amount of dissolved C that takes part in graphene formation in the subsequent cooling stage. Moreover, further growth parameters need to be explored such as working in atmospheric pressure and growth using different CH_4/H_2 ratios.

GDOES proved to be a good technique for the elements bulk analysis; however, the results need to be interpreted to concentration-depth scale, which would give more useful information about the diffusion coefficient and diffusion depth. This could be achieved by calibrating the GDOES machine using standard samples with known concentrations of the elements within interest.

The gas phase kinetic model presented in this work uses 36 chemical equations and 18 chemical species; furthermore, increasing the chemical equations and species would enable the model to cover a longer residence time until the thermodynamic equilibrium point was reached. The gap between the surface reactions model and the experimental results at higher pressure might be due to excluding the contribution of the other gas phase species. Therefore, broadening the assumption to include not only CH_4 but also other high concentration species is required to improve the surface reaction model at different growth pressures.

Finally, merging all the model parts, *i.e.* fluid flow, heat transfer, gas phase kinetics, and surface reactions in one single COMSOL file would be very useful to estimate the growth time. Using the new Apps feature in COMSOL allows the creation an easy application based on this work simulation, which will be available to everyone to use and improve effectively.

9. References

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