Chemical Vapor Deposition of Graphene on Prepatterned Catalyst

Master's thesis in Nanotechnology

Xiaotian Lin

DEPARTMENT OF SOME SUBJECT OR TECHNOLOGY

CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2024
www.chalmers.se

Master's thesis 2024

Chemical Vapor Deposition of Graphene on Prepatterned Catalyst

XIAOTIAN LIN

Department of Nanotechnology
Chalmers University of Technology
Gothenburg, Sweden 2024

Chemical Vapor Deposition of Graphene on Prepatterned Catalyst
Xiaotian Lin

Supervisor: Munis Khan
Examiner: Avgust Yurgens

Master's Thesis 2024
Department of Nanotechnology
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

Typeset in LaTeX
Printed by Chalmers Reproservice
Gothenburg, Sweden 2024

Growth and Characterization of CVD Graphene on Superflat Catalysts for Graphene Field-effect Transistors Hall and Biosensors
Xiaotian Lin
Department of Nanotechnology
Chalmers University of Technology

Abstract

This thesis explores the growth of high-mobility monolayer graphene on copper foils using Chemical Vapor Deposition (CVD), focusing on the influence of surface morphology and grain size of the copper substrate. Graphene's exceptional electrical, thermal, and mechanical properties make it a promising material for various advanced electronic applications, particularly in the development of graphene field-effect transistors (GFETs). However, achieving high-quality graphene with uniformity and minimal defects remains a significant challenge, primarily due to the variations in the copper substrate's surface characteristics.

In this work, we investigate the correlation between the copper foil's surface morphology and grain size and the quality of the graphene produced. The study employs low-pressure CVD (LPCVD) with methane as the carbon source, and hot-wall thermal CVD to precisely control the deposition environment. Key factors such as the copper substrate's crystallinity, smoothness, and catalytic properties are analyzed to optimize the growth process. The self-limiting nature of graphene growth on copper, facilitated by copper's low carbon solubility, is leveraged to achieve uniform monolayer graphene.

This project also includes the prepatterning method as one of the ways of controlling the alignment of nuclei, which is done based on maskless photo-lithography. By using prepatterning, patterned oxidation on copper foils can be achieved, the nucleation of graphene during CVD growth can only happen on the open areas where there's no oxide layer, which controls the position of nuclei.

Furthermore, this research aims to enhance the copper substrate preparation methods to improve graphene's mobility and overall quality, thus making it more viable for large-scale production. The outcomes of this study could contribute to advancing the scalability of high-performance graphene for industrial applications, particularly in the field of nanoelectronics.

Acknowledgements

I would like to express my sincere gratitude to Professor Avgust Yurgens and my supervisor Munis Khan for their invaluable guidance, support, and encouragement throughout the course of this research. Their expertise and insight have been instrumental in the completion of this work.

This thesis report uses Copilot to polish the sentences.

Xiaotian Lin, Gothenburg, September 2024

Contents

List of Figures

List of Tables

1

Introduction

1.1 Background

Graphene, a two-dimensional (2D) material composed of a single layer of carbon atoms arranged in a hexagonal lattice, has garnered significant attention due to its exceptional electrical, mechanical, and thermal properties. Among its most notable attributes are its high carrier mobility, mechanical strength, and thermal conductivity, making it a promising material for a wide range of applications, including flexible electronics, sensors, and energy storage devices[1]. To harness these properties effectively, it is crucial to develop reliable and scalable methods for producing high-quality graphene.

Chemical Vapor Deposition (CVD) is one of the most widely used techniques for synthesizing large-area, high-quality graphene[2][3]. This method involves the catalytic decomposition of carbon-containing precursor gases (such as methane) on a metal substrate, typically copper, under high-temperature conditions[2]. The choice of copper as a substrate is driven by its low carbon solubility, which promotes the formation of monolayer graphene and allows for easy transfer to other substrates[4].

However, the quality of graphene synthesized by CVD is highly dependent on the surface morphology and grain size of the copper foil. Surface morphology, including factors such as roughness and defect density, can significantly affect the nucleation and growth of graphene domains[5]. A smooth and defect-free copper surface promotes uniform graphene growth, reducing the likelihood of defects that can degrade the material's electrical and mechanical properties. Similarly, the grain size of the copper foil plays a crucial role in the growth process. Larger grain sizes are generally favorable as they reduce the number of grain boundaries, which can act as sites for graphene defects and impede carrier mobility[6].

Despite the potential of CVD-grown graphene, achieving high mobility and uniformity remains a challenge due to the inherent imperfections in commercially available copper foils. These foils often exhibit a wide range of grain sizes and surface roughness, leading to non-uniform graphene growth and the presence of grain boundaries that limit the overall performance of the material. Therefore, understanding and controlling the surface morphology and grain size of copper foils are critical for optimizing the growth process and producing high-quality graphene with enhanced properties.

1.2 Main purpose and aim of the project

The main purpose of this thesis is to find a way to grow high quality graphene with high mobility on copper foils using Chemical vapor deposition (CVD). In order to achieve this target, the nucleation and growth during CVD process should be controlled. In this project, the main method used is to control the nucleation center densities and positions.

There are a few factors affecting the nucleation density of graphene growth using CVD: temperature, gas concentrations, growth time, surface morphology and grain size of copper foils. The first step is to work with the surface morphology of copper foils. The method being used is electro-polishing, a surface polishing technique based on an electrolytic cell. In this process, different areas of the surface will have varying reaction rates, resulting in a uniformly smooth surface. The second step is to modify the grain sizes by averaging and slightly enlarging them. Annealing of the copper foil can be performed during the CVD process before nucleation and growth. Another method to improve grain structure is electroplating, which allows control of the grain nucleation orientation, a desirable condition for graphene growth. The third step is to control the nucleation position using photo-lithography. This allows nucleation to be restricted to the open areas. The total aim of the project is to prove these factors for graphene growth, and achieve controlled nucleation graphene growth.

2

Theory

2.1 Graphene and Graphene production techniques

2.1.1 Graphene

Graphene is a single atomic layer of carbon atoms arranged in a hexagonal pattern. It's the world's thinnest material with a thickness of only 0.334 nm[7]. Graphene has numerous distinguishing qualities due to its unique properties. It has a large specific surface area (2600 m^2/g)[8], high electron mobility (200,000 cm^2/Vs)[9], enhanced thermal conductivity (3000–5000 Wm/K)[10], extreme optical transparency (97.4%)[11], and exceptional mechanical strength, with Young's modulus of 1 TPa.

Focusing on its electrical properties, graphene has high electron mobility, which means that electrons can move through it very quickly. This property is crucial for many electronic applications[9]. The electrical attributes of graphene, such as carrier scattering, carrier concentration, charge polarity, quantum-capacitance enhanced doping, energy levels, transport mechanisms, and orbital hybridization of energy bands, can be influenced by a change in carbon's structural conformation, hybridization state, chemical potential, local energy levels, and dopant/interface coupling induced via functionalization or molecular interactions[12].

The Dirac electrons in graphene behave in unusual ways in tunneling, confinement, and the integer quantum Hall effect. The electronic properties of graphene stacks are discussed and vary with stacking order and number of layers.

In summary, graphene's unique electrical properties make it a promising material for future electronic devices.

2.2 Graphene Field-effect Transistors

Graphene Field-effect Transistors(GFET) is a type of transistor that utilizes graphene as its channel material. As silicon transistors approach their physical limits in terms of size and performance, researchers have turned to alternative materials like graphene[13].

The GFET has a thin graphene channel, usually tens of microns width, between the source and drain metal electrodes[14]. The gate controls how electrons respond and hence the channel's behavior.

GFETs have unprecedented sensitivity to a variety of external stimuli, including light (photo-sensing), magnetic fields (magnetic sensing), and biological molecules (bio-sensing), which can be exploited in a large variety of applications such as photo-sensing, magnetic sensing, and bio-sensing. When used in environmental sensors, this channel is typically exposed to permit the binding and detection of receptor molecules.

The two-dimensional structure of graphene has a number of benefits, over bulk semiconductors like silicon, used in standard FETs, such as High sensitivity, high carrier mobility, low noise, wide dynamic range, bio-compatibility, scalability, and flexibility. As the graphene in a GFET is only one carbon atom thick, the entire channel is now on the surface, which directly exposes the channel to any molecules present in the nearby environment[15].

GFET is used in biosensor fields nowadays, which requires high-quality graphene as the channel between two electrodes. Growing high-quality monolayer graphene with high speed and low cost is significant to many practical areas of use. By changing conditions, methods, and parameters, researchers can find better ways to produce graphene with high mobility more easily.

2.3 Chemical Vapor deposition

Chemical Vapor Deposition (CVD) is a widely used technique in materials science for producing, coatings, thin films, and high-purity materials[16]. This process plays an important role in various industries, including semiconductors, optics, aerospace, and energy, due to its ability to create uniform and high-quality layers of materials on a variety of substrates.

In principle, CVD is a chemical process that involves the deposition of a solid material from a vapor phase onto a substrate. The principle is mainly based on the reaction of volatile precursors—chemical compounds that contain the desired material—within a controlled environment[17]. These precursors are introduced into a reaction chamber, where they undergo chemical reactions, typically involving decomposition or chemical combination, to form a solid material that deposits onto the substrate.

The CVD process can be broken down into several key stages:

- Transport of reactant gases: The process starts with the introduction of reactant gases, or in other words precursors, into the reaction chamber. These gases are transported to the surface of the substrate by convection, diffusion, or a combination of both.

- Chemical reactions: When reaching the substrate, the reactant gases go through a series of chemical reactions. These reactions can occur either on the substrate surface or in the gas phase near the substrate. The properties and quality of these reactions depend on the specific CVD process being used. The primary objective is to produce a solid material that adheres to the substrate[18].
- Deposition of solid material: The chemical reactions result in the formation of a solid material, which nucleates and grows on the substrate surface. This deposition process continues until a uniform thin film or coating is achieved.
- Byproduct removal: The reactions often produce byproducts, which are usually in the form of gases. These byproducts need to be removed from the reaction chamber to prevent contamination and ensure the purity of the deposited material[19].

CVD is often used to make solid material with high uniformity and quality. By controlling the temperature, gas concentration, and time, monolayer material can be grown on the substrate, in this way, CVD is one of the best ways to grow graphene.

The kind of CVD that is being used in this project is hot-wall thermal CVD. The principle of the hot wall is, using a controlled current or voltage to heat up the heater(s) and control the temperature by controlling the voltage or overall power and sensing it with a thermal couple. The temperature needed in this thesis for graphene growth is close to the melting temperature of copper.

There are many kinds of CVD, such as atmospheric CVD(APCVD), low-pressure CVD(LPCVD), low-vacuum CVD(LVCVD). During this thesis, LPCVD is used to grow graphene on copper foils, since low gas concentration is needed, air should be avoided, but ultra-high vacuum takes too much time for a single sample.

The overall reaction of growing graphene is:

$$\mathrm{CH_4} \longrightarrow \mathrm{C} + 2\mathrm{H_2} \tag{2.1}$$

The concentration of methane plays an important role in the reaction and thus in the final quality of the graphene. Also, hydrogen is also needed to control the reaction rate and balance.

2.4 Graphene growth on copper

Copper (Cu) has become one of the most widely used substrates for growing monolayer graphene in the CVD process[20]. The choice of copper as a substrate is driven by several advantageous properties and characteristics:

- Low carbon solubility: Copper has a very low solubility for carbon at typical CVD growth temperatures (1000°C). This characteristic ensures that once carbon atoms are introduced onto the copper surface, they do not dissolve into the bulk of the copper but instead remain on the surface, where they can nucleate and grow into graphene. This property is crucial for achieving the

growth of high-quality monolayer graphene, as excess carbon in the substrate would lead to the formation of multi-layers or non-uniform graphene.
- Catalytic activity: Copper acts as a catalyst for the decomposition of carbon-containing precursor gases, which is methane in this thesis. The catalytic properties of copper help in breaking down the precursor molecules on its surface, releasing carbon atoms that then migrate across the surface and assemble into graphene. The catalytic efficiency of copper contributes to the uniform and controlled growth of graphene[21].
- Self-limiting growth: The low carbon solubility in copper also leads to a self-limiting growth mechanism for graphene. Once a monolayer of graphene is formed on the copper surface, it acts as a barrier that inhibits further carbon deposition, preventing the formation of additional layers. This self-limiting characteristic is vital for producing large-area monolayer graphene, which is desirable for many applications, particularly in electronics[22].
- Smooth surface and good crystallinity: Copper can be prepared with a relatively smooth surface and good crystallinity, which are important for the uniform growth of graphene. Smooth and well-ordered surfaces reduce the number of defects and irregularities in the graphene, leading to higher-quality material with fewer grain boundaries.
- Ease of transfer: Graphene grown on copper can be easily transferred onto other substrates for further processing or application. The weak interaction between graphene and copper facilitates the detachment of the graphene layer, typically using a chemical etching process that removes the copper substrate without damaging the graphene.
- Availability and cost: The final purpose of this method of growing graphene on copper foil is for mass production. Copper is an abundant and relatively inexpensive material, making it a cost-effective choice for large-scale production of graphene. This economic advantage is crucial for industrial applications where scalability and cost are significant factors.

The quality and characteristics of the copper substrate significantly influence the growth, structure, and properties of the resulting graphene. The main properties affecting graphene growth are shown below.

1. Surface morphology:
    - Smoothness: A smoother copper surface generally leads to the growth of graphene with fewer defects and a more uniform monolayer. Rough or uneven surfaces can introduce stress, defects, and non-uniformities in the graphene layer.
    - Step edges and defects: Step edges on the copper surface can act as nucleation sites for graphene growth. While controlled step edges can promote uniform growth, uncontrolled or excessive step edges can lead to multi-layer graphene or defective areas.
2. Grain size:
    - The grain size of the copper substrate has a direct impact on the size of the graphene domains. Larger copper grains tend to produce larger graphene domains with fewer grain boundaries, which are critical for achieving high electrical conductivity and mechanical strength in graphene.

- Polycrystalline copper: If the copper substrate is polycrystalline, with multiple grains of different orientations, the resulting graphene will have grain boundaries where the graphene domains meet. These grain boundaries can degrade the electrical, mechanical, and thermal properties of the graphene.

3. Crystallographic orientation:
    - The crystallographic orientation of the copper grains influences the alignment and orientation of the graphene lattice. Certain crystallographic planes, such as the (111) plane, are more favorable for the epitaxial growth of graphene with minimal defects. A well-aligned graphene lattice with the substrate leads to better electrical and structural properties.
4. Impurities and contaminants:
    - The presence of impurities or contaminants on the copper surface can adversely affect the growth of graphene by introducing defects or by promoting non-uniform nucleation. Ensuring high-purity copper and clean processing conditions is essential for producing high-quality graphene.

2.5 Mask-less photo-lithography

Photo-lithography is a technique in micro-fabrication that uses light to transfer geometric patterns from a photo mask to a light-sensitive chemical photo-resist on a substrate. This process is integral to the manufacturing of semiconductor devices, printed circuit boards, and various other microstructures.

Maskless photo-lithography was used in the thesis. In conventional photo-lithography, a mask is in physical contact with the sample. However, these masks can be a source of errors and defects, particularly when working with very small geometries or when dealing with substrates like copper foils that may not be perfectly flat or uniform.

Working principle of maskless lithography:

- Digital patterning: Instead of using a physical photo-mask, maskless smart-print utilizes a digital mask or pattern that is generated and controlled by software. This pattern can be directly projected onto the substrate using a variety of imaging technologies, such as laser or digital micro-mirror devices (DMDs). The digital nature of the pattern allows for real-time adjustments and modifications without the need for physical mask fabrication.
- Direct writing: The technology often involves direct writing techniques where the pattern is created by a focused laser or other energy sources that interact with the substrate or a photo-resist layer. This method is akin to how a laser directly engraves or modifies a material but with much higher precision at the microscale or nanoscale level. The lack of a physical mask prevents issues related to mask alignment and wear.
- Substrate Positioning and Control: The substrate is positioned using precise motorized stages, ensuring that the pattern is accurately transferred onto the desired areas. This control allows for high-resolution patterning even on substrates with complex geometries.

There are several reasons for choosing Maskless Smart-print instead of a photo-lithography with a photo-mask, The reasons are shown below.

- Flexibility in design: Maskless allows for rapid customization of designs without the need for new photo-masks. This flexibility is crucial in prototyping and small-scale production where design changes are frequent. For copper foils used in custom PCBs or other electronic components, this capability significantly reduces time and costs.
- High precision and resolution: The direct writing process in maskless lithography can achieve high resolution.
- Adaptability to substrate variations: Copper foils may exhibit surface variations, such as slight warping or uneven thickness. Traditional photo-lithography, which relies on physical masks, potentially leading to alignment errors and defects. Maskless lithography's ability to adjust the focal length in real time allows it to accommodate these variations, ensuring consistent patterning even on uneven substrates.
- No need for physical masks: By eliminating physical masks, markless lithography reduces the risk of defects associated with mask misalignment, wear, or contamination. This is particularly beneficial for graphene on copper foils, where a physical contact with the mask can damage the graphene.
- Cost for small batches: Producing physical masks for photo-lithography can be costly, especially for small production runs or one-off designs. Maskless lithography removes this cost barrier, making it economically viable to produce small batches or prototypes with complex patterns on copper foils.

3

Methods and materials

3.1 Four-point measurement

Four-point measurement is used to test the mobility, sheet resistance, and electron density.

The process of the Hall effect test is shown below:

- Four-Probe Configuration: Four electrical contacts (probes) are attached to the sample. These probes are usually made of a conductive material like gold or silver. The probes are positioned in a linear arrangement along the length of the sample.
- Current Application: A constant current is passed through the sample using the two outer probes. This current creates a uniform current density across the sample. The current source is carefully controlled to ensure stability and accuracy.
- Magnetic Field Application: A perpendicular magnetic field is applied to the sample. This magnetic field is typically generated using an electromagnet. The strength of the magnetic field is precisely controlled and measured.
- Hall Voltage Measurement: The Hall voltage is measured across the two inner probes. This voltage is generated due to the deflection of charge carriers (electrons or holes) by the magnetic field.
- The measured Hall voltage is used to calculate the Hall coefficient R_H, which is given by the formula:

  $$R_H = \frac{V_H \cdot t}{I \cdot B} \tag{3.1}$$

  where V_H is the Hall voltage, t is the thickness of the sample, I is the current, and B is the magnetic field strength. The Hall coefficient is then used to determine the carrier concentration n and mobility μ of the semiconductor material, where e is the elementary charge and σ is the electrical conductivity of the sample:

  $$n = \frac{1}{R_H \cdot e} \tag{3.2}$$

  $$\mu = \frac{R_H \cdot \sigma}{e} \tag{3.3}$$

3.2 Photo-lithography

Photo-lithography is a technique typically used for making micron-sized structures. The first step is spin-coating: photo-resist is placed on the sample surface by spin-coating for a specific rate and time. There are two kinds of photo-resists, for the first one, the photo-resist after exposure/printing can be washed away by the corresponding developer, keeping the area without exposure, which is called positive photo-resist, the other one is the contrary, which is called negative photo-resist.

The resolution of the exposure or printing process is determined by the wavelength of the light source, similar to optical microscopy. To expose or observe a feature, the wavelength of the light must be smaller than the feature's size. This technique allows specific areas to be protected from etching or enables selective material deposition in designated regions. In this project, only single-layer photolithography is required, primarily to control nucleation areas during the CVD process.

3.3 Scanning Electron Microscopy

Scanning Electron Microscopy(SEM) is a kind of electron microscope observing the micro-structure of a sample by scanning the surface with focused electron beams. The secondary electrons emitted by the sample atoms are used, which is suitable for the thesis since only surface morphology is important for this project.

3.4 Raman Spectroscopy

Raman spectroscopy is used to determine vibration modes of molecules. For this thesis, by measuring the intensities and ratios between intensities peaks, one can determine the quality of the graphene on the sample spot detected.

In this case, one can use the mapping function of Raman spectroscopy, by setting the step distance and range, a series of spots on the sample can be detected. By this way, the total quality, quality separation, and graphene distribution for specific designed pattern can be detected.

3.5 Different kinds of copper foils

The first kind of copper is commercial copper foil, which is not smooth at the micro level. There are many vertical defects on the foil surface mainly caused by mechanical drawing. Also, there should be many grains inside the foil as it is in bulk copper.

Figure 3.1: An optical microscope image of commercial copper-foil surface.

The second kind of copper is electro-polished copper foil. The principle of electro-polishing is: By using an electrolytic cell, the copper foil is placed at the anode and a conductor, which can also be copper, is placed at the cathode. This setup allows the copper foil to be etched. The thickness of the foil influences its resistance, which in turn affects the current and reaction speed. As a result, the height differences on the surface of the foil are reduced, making the sample smoother. By using the electro-polishing technique, surface defects can be removed or decreased, making the copper foil surface smoother at the micro level. Since electro-polished copper is based on commercial copper foil and only the sample surface is polished, the grain size and concentration are still the same as commercial foils.

The third type of copper is electroplated copper foil. Electroplated copper foil is also produced using electrolytic cells. However, the process differs from that used for electro-polished copper foil. On the contrary, the electroplating copper foil is made by copper growth the cathode conductor surface, a copper anode is used to provide copper ions, which will be reduced to copper on the cathode. The basic principle behind this method is to deposit a thin layer of copper onto a superflat substrate, typically a silicon wafer, which acts as a template. The flatness of the silicon wafer ensures that the copper deposited inherits the smoothness of the surface. By carefully controlling the electroplating process, a thin copper layer is initially deposited, which is then thickened through further electroplating. After achieving the desired thickness, the copper foil is stripped from the template, yielding an ultra-flat copper surface.

4

Results and discussion

4.1 Standard growth on commercial copper foils

The influence of the ratio between methane and hydrogen during CVD is the first factor of interest. In this case, the concentration of the hydrogen is fixed while the concentration of the methane is changed for different ratio.

Firstly, a ratio from Munis Khan's article[23] is used as the standard ratio, which is: methane (5% CH_4 in argon, 120 sccm), hydrogen(60 sccm), since this ratio is proved that can be used to make high-quality graphene, it is easier to observe the influence of changing the ratio.

The ratios are set based on the standard ratio:
- 120 sccm (100% standard ratio)
- 96 sccm (80% standard ratio)
- 72 sccm (60% standard ratio)
- 48 sccm (40% standard ratio)
- 24 sccm (20% standard ratio)

The rest conditions, such as annealing temperature, growth temperature, time recipes, are the same for all ratio sets.

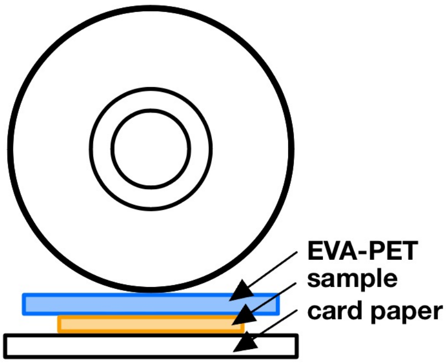

Figure 4.1: An image showing the lamination process using lamination machine.

As shown in Figure 4.1, after growing graphene on copper foils, graphene is transferred to EVA-PET by lamination. The EVA-PET can be adhesive when it is heated to a certain temperature, which is 125°C for the sample in this project. The copper foil is attached to the sticky side of EVA-PET, with a piece of protection card paper on the other side to prevent sticking on the machine. The roller in the lamination machine can provide stress and heat at a set temperature to ensure full attachment. After that, etching away the copper foils by 30% nitric acid, graphene is transferred to EVA-PET.

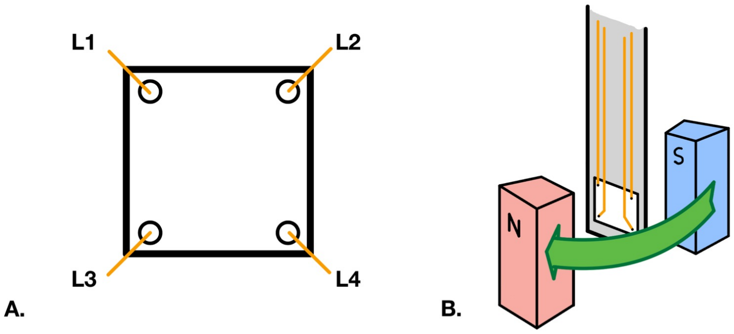

Figure 4.2: An image showing the Hall effect test process using four-point measurement. A. Positions of four probes connecting the sample, The probes should be at the corners of the sample to have a more accurate measurement. B. The magnetic field rotates perpendicular to the sample plane. During rotation, measurement points are set at consistent angular intervals. Increasing the number of points per rotation enhances the accuracy of the measurement.

The four-point measurement is used for the characterization of graphene, by using four-point measurements, sheet resistance, mobility, and electron density can be measured. These properties can show the quality of graphene transferred to EVA-PET. The results of the four-point measurement are shown below as Table 4.1. A standard recipe is used to gain the best mobility of graphene on commercial copper foils, which is 15 minutes of annealing; and 3 minutes nucleation with 30 sccm of 5% methane in Argon, and 6 minutes growth with 120 sccm of 5% methane in Argon[23]. The annealing process can improve the grain condition and enlarge the grain size, which is better for graphene growth.

Table 4.1: Measured the average mobility for different methane concentrations.

$Mobility$	CH_4	μ(mobility)[cm^2/Vs]
1	100%	8280
2	80%	5310
3	60%	3490
4	40%	3770
5	20%	4170

From Table 4.1, It can be seen that: when the concentration of methane is smaller than the standard concentration, the mobility generally increases with the increasing methane concentration.

4.2 Patterned growth on commercial copper foils

After growing graphene samples on standard non-patterned copper foils, the mobility, sheet resistance, and electron density of these samples are tested. The next step is to create graphene samples with a patterned design to control the growth of graphene. This is the main objective of the thesis.

The purpose of the design is mainly to control the nucleation and locations in order to control the final growth to form a uniform monolayer graphene. Before designing the pattern, one should first understand the shape and formation mechanism of graphene nuclei. A graphene nucleus is shown in the Figure 4.3.

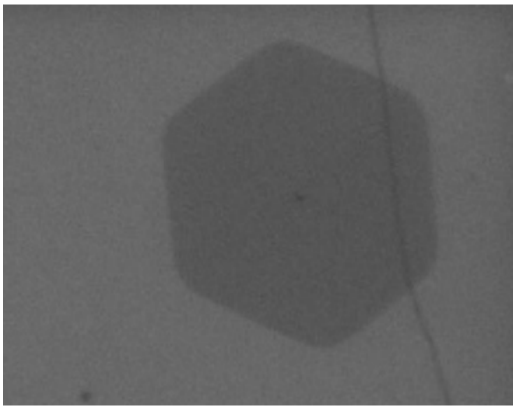

Figure 4.3: An SEM image of graphene nuclei.

As shown in the figure, the graphene nucleus normally has the shape of standard hexagons, The growth is uniform in all directions from the nucleus, resulting in regular hexagonal shapes. According to this mechanism, the pattern should be designed in order to keep all the edges of hexagons parallel to each other. In this way, graphene from different nuclei can have a higher probability of connecting to each other. The design is shown in Figure 4.4

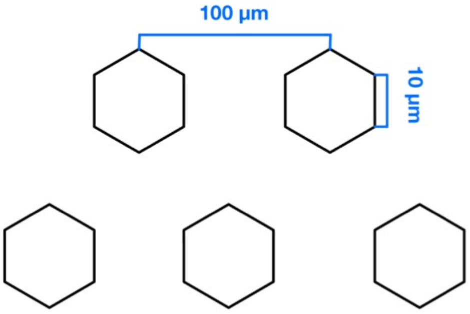

Figure 4.4: An image showing the designed pattern used in this project.

In order to make the copper foils with a patterned design, firstly the designed pattern is made by AutoCAD. After that, a file converter is used to convert the pattern files to form of files that can be directly read by the maskless photo-lithography machine.

The next step is to spin the photo-resist on the copper foils. Before spinning, copper foils should be fixed to achieve a relatively flat surface, which is significant for the focus before printing. In this project, silicon wafer pieces and thermal-release tapes are used for this purpose. The thermal-release tape is a double-sided adhesive, it won't react with any chemicals used during the process; thermal-release tape becomes non-adhesive at certain temperatures, which eases the removal of the foil from the wafer after the photo-lithography.

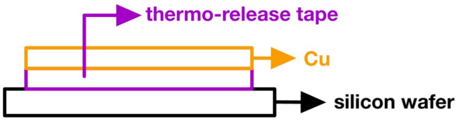

Figure 4.5: An image showing the Cu/thermal-release tape/silicon wafer.

The detailed photo-resist spin-coating process is as follows: First, a thermal-release tape with a release temperature of 170°C is selected. After cleaning, the copper foil is attached to one side of the tape. Next, the silicon wafer surface is cleaned with acetone, and the other side of the thermal-release tape is pressed onto the wafer using a clean roller. This completes the preparation step. Afterward, the spin-coating machine is turned on, and the heater is set to 95°C for soft baking after the spin-coating.

The process begins by selecting a suitable sample holder. Attach the holder to the machine, place the sample on the holder, and align its center with the vacuum hole at the center of the holder. Turn on the vacuum pump, which will secure the sample in place. Check the pressure reading on the screen to ensure it falls within the safety range.

Next, select the photo-resist—S1813, a positive photo-resist, is used in this project. Using a disposable pipette, apply about 3 ml of photo-resist at the center of the sample. Close the protection lid and set the spin-coating machine to a recipe of 60 seconds at 4000 rpm. Start the spin-coating process. Once spinning is complete, transfer the sample to a hot plate for baking at 95°C for 1 to 1.5 minutes. Allow it to cool to room temperature, then inspect the surface for smoothness. After these steps, the sample is ready for printing.

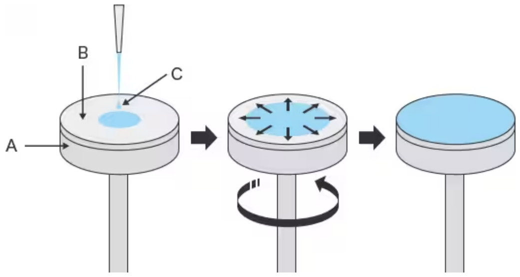

Figure 4.6: An image showing the principle of spin coating process[24].

To allow the system and lamp to fully warm up, the maskless printing machine should be switched on about two minutes before use. Place the sample at the center of the sample stage and select a 10x objective lens. Choose the exposure file, ensuring the UV filter is closed. Before exposure, the stage needs to be leveled, so activate focus mode.

Begin by moving the stage and aligning the exposure spot to the top-left corner of the desired exposure area. Adjust the stage height to set the focus. Next, align the exposure spot to the top-right corner and use the first adjustment screw to refine the focus. Then, align the exposure spot to the bottom-left corner and adjust the focus using another screw. Repeat these steps until the entire sample is in focus and properly aligned.

Once the alignment is complete, return the exposure spot to the top-left corner, which will serve as the starting point. Exit focus mode, remove the UV filter, and activate the exposure mode.

After the exposure, which usually takes 20-40 minutes, the exposure is done, and the filter should be pulled back. The sample is taken to be developed. A kind of developer should be chosen, which is MF319 in this project, the sample should be placed inside the developer for one minute, the exposure area should be etched, and after washing it with DI water, the photo-lithography processes are done.

In the first case, the hexagon areas are etched. The sample is heated to 100°C for half an hour in an oven or hot plate. Afterward, the hexagonal areas will be covered with uniform oxide layers. These layers prevent nucleation inside the hexagons during the growth process. Nucleation will instead begin at the edges of the hexagons. In principle, the nucleation will follow the edges of the designed patterns, as the edges of the oxide layers act as nucleation centers.

In the second case, the hexagon areas are kept and the rest areas are etched. The sample is also heated to 100°C for half an hour in an oven or hot plate. After that, the hexagon areas will be opened and the rest will be covered with uniform oxide layers. In this way, nucleation will be confined within the hexagons, which, in theory, should guide the final growth as expected.

The designed pattern could prevent the final graphene areas from connecting to each other, which will cause the overall graphene non-conductive. For non-conductive material, four-point measurement cannot be operated since no current can go through the material. Because the large-scale four-point measurement cannot be used to microstructure, SEM should be used to characterize the microstructure and the growth condition, which is shown in Figure 4.7. This figure shows an SEM image of a sample of patterned graphene growth on copper foil with hexagon areas as open areas. The hexagon areas are kept during the exposure and therefore become the open areas without oxide layers. It can be seen that the graphene is grown inside the hexagon, since the graphene has lower conductivity than the copper foil substrate, the hexagon areas are darker.

After the oxidation process, the photo-resist should be removed by acetone, and the sample should be cleaned with DI water, the CVD after that has the same process.

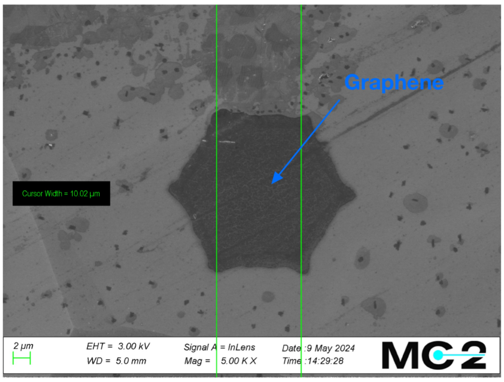

Figure 4.7: An SEM image of a CVD growth graphene on a copper foil with the designed pattern with hexagons kept.

The graphene is highly condensed in the hexagon area, which is caused by the high nucleation density, which can not be avoided when commercial copper foils are used. Because of the high defect density and small grain sizes, the nucleation density cannot be decreased to the desired level on commercial copper foils, in this way, different kinds of copper foils with less nucleation center should be used to avoid this.

4.3 Electro-polished copper foil preparation and standard CVD

Electropolished copper foils should be used as a better choice with less nucleation density. At first, electro-polished copper foils should be prepared.

The raw materials used to prepared electro-polished copper foils are also commercial copper foils but with larger thickness.

Before the electro-polishing, the electrolyte should be prepared. Firstly, add 35ml of DI water to a beaker, after that, add 165ml of 85% phosphoric acid to the same beaker, then stir the solution for one minute to fully dissolve phosphoric acid, forming a 200ml solution.

As shown in Figure 4.8, a thin copper piece is used as the cathode in this project. A current generator is used as the voltage source. Connect the copper piece to the cathode of the current generator, put the copper piece into the beaker with the electrolyte solution, with most part of the copper piece in the electrolyte. Choose a piece of commercial copper foil with roughly two times thicker than the commercial copper foil being used for CVD for the previous case, clean it with acetic acid for one minute. After removing acetic acid left on the copper foil with DI water and drying it with nitrogen gas, the copper foil is connected to the anode of the current generator, with one of the surfaces facing the cathode. The electrolysis process used in this project is voltage-controlled, the voltage is fixed to 1.3V. The electro-polishing process will take 40 minutes. After the polishing process, the electrolyte left on the copper foil should be cleaned by acetic acid and DI water.

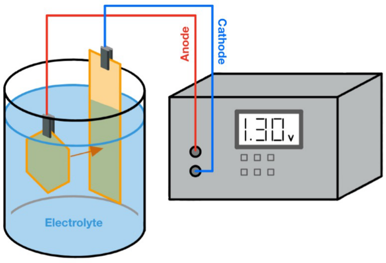

Figure 4.8: An image showing the electro-polishing process.

After the preparation of electro-polished copper foils, the standard CVD recipe should be operated on the foils and checked for mobility. The overall CVD process should be the same as the operation of the commercial copper foils, the four-point measurement process is also the same, the resulting average mobility is 9200, which is obviously higher than the mobility obtained in graphene growth on commercial foil without electro-polishing. By this, it can be seen that the graphene growth on the electro-polished copper foils is better than on the commercial copper foils, which fits the theories of the morphology difference and corresponding defect density.

Also, SEM images are obtained to characterize the graphene quality. As shown by Figure 4.9, it can be seen that the uniformity is better than the graphene growth on commercial copper foils.

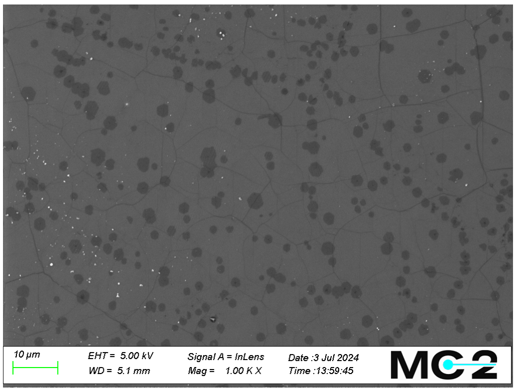

Figure 4.9: An SEM image of graphene growth on an electro-polished copper foil with standard recipe.

4.4 Electro-polished CVD with designed pattern

After growing standard graphene on electro-polished copper foils, a recipe should be found to grow the graphene with zero conductivity, which would have much lower nucleation density, and the graphene will be non-continuous too. The way chosen for finding this recipe is dichotomy, one of the boundary conditions is the standard recipe, which would have the largest mobility, the other boundary condition should have a really low methane concentration in the precursor gases, making sure that it is not possible for continuous graphene to form, which should have no overall conductivity. Figure 4.10 shows an SEM image of graphene growth on an electro-polished copper foil with a considerably low methane concentration recipe. It can be seen that the graphene grains are in hexagon shapes. The grains are also isolated, resulting in a discontinuous material that is non-conductive.

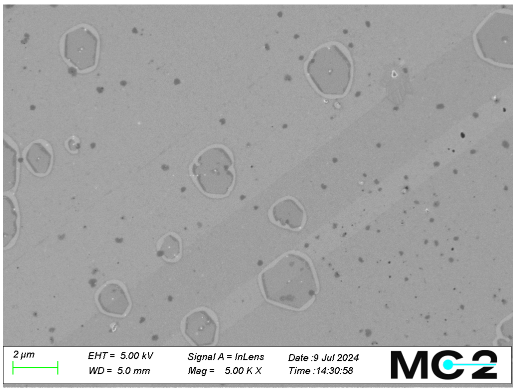

Figure 4.10: An SEM image of graphene growth on an electro-polished copper foil with a considerably low methane concentration recipe.

Because of the machine issues, the exact low methane concentration boundary condition has not been found during this thesis, a small range, instead, was confirmed. The recipe corresponding to the boundary condition has the methane concentration during nucleation and growth between 5 and 7 sccm. Figure 4.11 shows graphene growth on an electro-polished copper foil using a specific low methane concentration recipe. The graphene grains can be seen starting to connect and merge. This indicates that the recipe used here represents a boundary condition between continuous and non-continuous graphene growth.

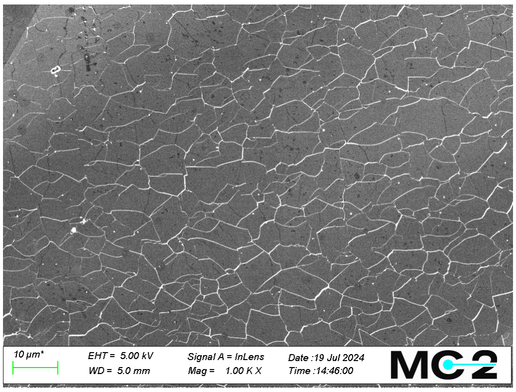

Figure 4.11: An SEM image of graphene growth on an electro-polished copper foil with a specific low methane concentration recipe.

According to the plan, after finding the correct low methane concentration recipe, patterned photo-lithography on electro-polished copper foils, which is the same as the process for commercial copper foils, should be made to control the nucleation of graphene during the CVD process. Due to the smoother surface, the defect density on copper is lower, therefore the nucleation density is lower, there should be isolated graphene in the open areas. By further controlling the recipe, lower nucleation density can be reached, in ideal conditions, single nuclei in every single open hexagon can be reached, which is the expected result.

5

Conclusion

The graphene growth on copper foil is highly related to the grain sizes and surface morphology of the copper foil substrates. Smoother copper foil surfaces have fewer defects, since graphene nucleation is expected at defects in copper, less nucleation density for graphene growth; the larger the grain sizes, the better for large-area graphene growth, the grain orientation can also affect the graphene growth, with crystallographic planes as the (111). Graphene growth is better on electro-polished copper foils compared to commercial copper foils. According to theory, electroplated copper foils should have an even better surface condition and significantly larger grain sizes. Additionally, the natural nucleation centers on electroplated copper foils are much smaller, making it easier to create artificial nucleation centers for controlled growth. This thesis hasn't reached the desired result of controlled graphene growth, but the processes show the trend of lowering nucleation density, future work should be done for further research.

6

Reference

[1] K. S. Novoselov et al. "Electric Field Effect in Atomically Thin Carbon Films". In: *Science* 306.5696 (2004), pp. 666–669. DOI: `10.1126/science.1102896`.

[2] Xuesong Li et al. "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils". In: *Science* 324.5932 (2009), pp. 1312–1314. DOI: `10.1126/science.1171245`.

[3] Sukang Bae et al. "Roll-to-roll production of 30-inch graphene films for transparent electrodes". In: *Nature nanotechnology* 5.8 (2010), pp. 574–578. DOI: `10.1038/nnano.2010.132`.

[4] Alfonso Reina et al. "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition". In: *Nano Letters* 9.1 (2008), pp. 30–35. DOI: `10.1021/nl801827v`.

[5] Ivan Vlassiouk et al. "Role of Hydrogen in Chemical Vapor Deposition Growth of Large Single-Crystal Graphene". In: *ACS Nano* 5.7 (2011), pp. 6069–6076. DOI: `10.1021/nn2003935`.

[6] Robert S. Weatherup et al. "In Situ Characterization of Alloy Catalysts for Low-Temperature Graphene Growth". In: *ACS Nano* 8.8 (2014), pp. 8626–8637. DOI: `10.1021/nn502946v`.

[7] Andre K Geim and Konstantin S Novoselov. "The rise of graphene". In: *Nature materials* 6.3 (2007), pp. 183–191. DOI: `10.1038/nmat1849`.

[8] Daniel R Dreyer et al. "The chemistry of graphene oxide". In: *Chemical Society Reviews* 39.1 (2010), pp. 228–240. DOI: `10.1039/B917103G`.

[9] Kirill I Bolotin et al. "Ultrahigh electron mobility in suspended graphene". In: *Solid state communications* 146.9-10 (2008), pp. 351–355. DOI: `10.1016/j.ssc.2008.02.024`.

[10] Alexander A Balandin et al. "Superior thermal conductivity of single-layer graphene". In: *Nano letters* 8.3 (2008), pp. 902–907. DOI: `10.1021/nl0731872`.

[11] Rahul R Nair et al. "Fine structure constant defines visual transparency of graphene". In: *Science* 320.5881 (2008), pp. 1308–1308. DOI: `10.1126/science.1156965`.

[12] AH Castro Neto et al. "The electronic properties of graphene". In: *Reviews of modern physics* 81.1 (2009), p. 109. DOI: `10.1103/RevModPhys.81.109`.

[13] Frank Schwierz. "Graphene transistors". In: *Nature nanotechnology* 5.7 (2010), pp. 487–496. DOI: `10.1038/nnano.2010.89`.

[14] Yu-Ming Lin et al. "100-GHz transistors from wafer-scale epitaxial graphene". In: *Science* 327.5966 (2010), pp. 662–662. DOI: `10.1126/science.1184289`.

[15] Xiao Huang et al. "Graphene-based biosensors". In: *Materials Today* 14.7-8 (2011), pp. 424–432. DOI: `10.1016/S1369-7021(11)70161-1`.

[16] Klaus J Bachmann. "Handbook of chemical vapor deposition: principles, technology, and applications". In: *Noyes publications* (1999).

[17] Hugh O Pierson. *Handbook of chemical vapor deposition (CVD): principles, technology and applications.* Vol. 2. William Andrew, 1999.

[18] Sanghyo Lee, Kwangyeol Lee, and Youngho Kim. "Effect of substrate roughness and grain structure on the growth of graphene on Cu by chemical vapor deposition". In: *Nano letters* 12.5 (2012), pp. 2374–2378. DOI: `10.1021/nl300133z`.

[19] Guangyu Sun et al. "Fabrication of aligned carbon nanotube and graphene electrodes for high-performance flexible supercapacitors". In: *Advanced Materials* 18.8 (2006), pp. 1032–1036. DOI: `10.1002/adma.200502792`.

[20] Xuesong Li et al. "Large-area synthesis of high-quality and uniform graphene films on copper foils". In: *Science* 324.5932 (2009), pp. 1312–1314. DOI: `10.1126/science.1171245`.

[21] Peter Sutter, Jerzy T Sadowski, and Eli A Sutter. "Graphene growth on polycrystalline Ru thin films". In: *Journal of the American Chemical Society* 131.10 (2009), pp. 3346–3352. DOI: `10.1021/ja808192d`.

[22] Jianping Wu et al. "Wafer-scale synthesis of graphene by chemical vapor deposition and its application in hydrogen sensing". In: *Sensors and Actuators B: Chemical* 161.1 (2012), pp. 875–879. DOI: `10.1016/j.snb.2011.10.022`.

[23] Munis Khan et al. "High Mobility Graphene on EVA/PET". In: *Nanomaterials* 12.3 (2022). ISSN: 2079-4991. DOI: `10.3390/nano12030331`. URL: `https://www.mdpi.com/2079-4991/12/3/331`.

[24] *Spin Coating Method and Principle | Types of Coaters and Coating Methods.* `https://www.keyence.com/ss/products/measure/sealing/coater-type/spin.jsp`. [Online; accessed 16-August-2024]. n.d. URL: `https://www.keyence.com/ss/products/measure/sealing/coater-type/spin.jsp`.

DEPARTMENT OF SOME SUBJECT OR TECHNOLOGY
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden
www.chalmers.se