Chemical Vapor Deposition Growth of Wafer-Scale Highly Crystalline Two-Dimensional Materials

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ABSTRACT

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Junzhu Li

As a promising advanced two-dimensional (2D) material with remarkable physical-chemical properties, graphene shows considerable potential applications in semiconductor nanodevices and many other fields. Chemical vapor deposition (CVD) has been widely used to synthesize 2D materials, including graphene. To date, many efforts have been made on the CVD growth of higher quality graphene film on arbitrary substrates (e.g., metals and insulators). However, it remains very challenging due to the underlying complex physical mechanisms and numerous influence factors in the CVD growth process. Furthermore, the growth of inch-scale high-quality graphene on insulating substrates is desirable for electronic and optoelectronic applications, but remains challenging, so far, due to the lack of metal catalysis.

In this dissertation, we reveal the existence of a fractal-growth-based mechanism in the CVD synthesis of several 2D materials, to which we build a 2D-DLA model based on an atomic-scale growth mechanism and the traditional fractal theory. The strength of this model is validated by the good correlation between theoretically simulated data and experimental results obtained from the CVD growth of graphene, hBN, and TMDs. By applying the 2D-DLA model and carefully tuning
the crucial factor of the single-domain net growth rate, we synthesize various fractal-morphology high-quality single-crystal 2D materials, achieving, for the first time, the precise control of the 2D-material CVD growth. Our work lays the theoretical foundation for the precise adjustment of the morphologies and physical properties of 2D materials, which is essential to the use of fractal-shaped nanomaterials for the fabrication of new-generation neural-network nanodevices.

Based on the deeper understanding of the CVD growth mechanism, we have successfully achieved the synthesis of wafer-scale adlayer-free ultra-flat single-crystal monolayer graphene on sapphire substrates. We converted polycrystalline Cu foil placed on Al₂O₃(0001) into single-crystal Cu(111) film via annealing, and then achieved epitaxial growth of graphene at the interface between Cu(111) and Al₂O₃(0001) by a multi-cycle plasma-etching-assisted CVD method. We have also successfully proposed a model to formulate the growth mechanism of the single-crystal monolayer graphene at the interface. This work breaks a bottleneck of synthesizing wafer-scale single-crystal monolayer graphene on insulating substrates and could contribute to next-generation graphene-based nanodevices.
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<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DLA</td>
<td>Diffusion-limited aggregation</td>
</tr>
<tr>
<td>D-SIMS</td>
<td>Dynamic secondary ion mass spectrometry</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect transistor</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FLG</td>
<td>Few-layered graphene</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half-maximum</td>
</tr>
<tr>
<td>hBN</td>
<td>hexagonal boron nitride</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>IPF</td>
<td>Inverse polar figure</td>
</tr>
<tr>
<td>LEED</td>
<td>Low-energy electron diffraction</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>Molybdenum disulfide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-pyrrolidone</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SD-NGR</td>
<td>Single-domain net growth rate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunneling microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TMDs</td>
<td>Transition metal dichalcogenides</td>
</tr>
<tr>
<td>XRD</td>
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Chapter 1 Introduction

1.1 Introduction of Two-dimensional Materials

1.1.1 Graphene

Since the discovery of fullerenes (C\textsubscript{60}) in 1985 and carbon nanotubes in 1991\textsuperscript{1,2}, carbon nanomaterials have been the focus of nanoscience research\textsuperscript{3}. Various carbon nanocrystals, C\textsubscript{60}, carbon nanotubes, and carbon nanocones have been reported. Graphene, as a single-layered carbon-atom structure, was firstly discovered in 2004 by Geim and Novoselov, who were awarded the 2010 Nobel Prize for Physics\textsuperscript{4}. In the past, graphene and two-dimensional (2D) materials were presumed to be inexistent. Moreover, the Mermin–Wagner theory suggested that thermal perturbations destroy long-range-ordered 2D crystals at room temperature owing to their thermodynamic instability\textsuperscript{5}. This theory was confirmed by several experiments and widely accepted. Thus, when single-layer graphene was successfully prepared in a laboratory, the scientific community was considerably excited. It is now commonly believed that the surface of graphene is not perfectly flat but has a microscopically distorted 2D structure with nanoscale folds, as shown in Figure 1.1\textsuperscript{6}.

Figure 1.1 (a) Graphene with flat surface. (b) Graphene with wrinkled surface.\textsuperscript{6}
Graphene is a 2D crystal composed of carbon atoms forming a hexagonal honeycomb lattice through sp$^2$ hybridization. The three outer electrons of each carbon atom form sp$^2$ hybridization $\sigma$-bonds, and the angle between two adjacent bonds is 120°, leaving one electron to form a conjugated $\pi$-bond with the remaining fourth electron of the carbon atom. The graphene C–C bond has a length of approximately 0.142 nm. The $\sigma$-bonds are important for producing the graphene skeleton, which is extremely strong and forms a stable hexagonal structure. The conductive process considerably relies on $\pi$-bonds running perpendicular to the graphene crystal plane. Graphene can be considered as the fundamental structure of all carbon nanomaterials.

1.1.2 Hexagonal Boron Nitride

In recent years, another 2D planar-structured material has received increasing attention. Hexagonal boron nitride (hBN), called "white graphene" due to its graphene-like structure, is a material with layers bound together by van der Waals forces and composed of nitrogen and boron atoms. Different from the semi-metallic nature of graphene, hBN is used an insulator due to its wider forbidden band of 5.97 eV. The strong B–N covalent bond provides the hBN film outstanding thermal stability and chemical inertness. The film also gains excellent in-plane mechanical strength and thermal conductivity that are comparable to those of graphene. Graphene can only withstand temperatures up to approximately 600 °C in air, whereas hBN remains stable at 1000 °C. In
addition to having a narrow absorption peak in the deep ultraviolet (UV) region, hBN is completely transparent in the visible range. Hence, it has potential for various applications, such as UV emitters, transparent films, and insulating protective layers.22

As a 2D material with a considerably flat surface, hBN has extremely few dangling bonds and charge traps. Hence, it is an ideal substrate for carrying other 2D materials.26-32 The electron mobility of graphene on single-crystal hBN has been reported to be as high as its electron mobility in suspended state. This is attributed to the atomic-level smoothness of hBN and absence of dangling bonds that can eliminate the effect of surface charge.33 The hBN monolayer has high phonon energy and better matching with graphene lattice; consequently, its use as a substrate enables graphene to attain maximum electron mobility.33,34 In addition, hBN can be used for DNA small-pore sequencing and filtering as well as hydrogen isotope sieving.35,36 Accordingly, 2D crystalline materials, such as hBN, are highly valued by various related disciplines and industrial fields, leading to a rare upsurge in research and promoting multidisciplinary crossover and development.

### 1.1.3 Other 2D Materials

In addition to graphene and hBN, 2D transition metal dichalcogenides (TMDs) have attracted considerable interest from the 2D materials community. TMDs consist of more than 40 compounds. Their general formula is MX$_2$, where M denotes groups 4–7 of transition metals, and X is a chalcogenide element (such
as S, Se, and Te). Because of their high electron mobility and excellent optical, electrical, chemical, acoustic, and mechanical properties, TMD-layered materials have gained considerable interest. A typical example of these materials is molybdenum sulfide (MoS\(_2\)). Monolayer MoS\(_2\) compared with conventional silicon materials has a smaller volume and lower dielectric constant. It has a 1.8-eV direct bandgap and an excellent carrier mobility owing to its quantum-limited domain effects. Further, it has excellent electrical, optical, and semiconductor properties, such as high Seebeck coefficient, considerable photoconductivity response, significant exciton effect, high mechanical strength, and tunable bandgap. The foregoing renders MoS\(_2\) a material of choice for next-generation nanomicroelectronic devices.

### 1.2 Synthetic Methods

#### 1.2.1 Mechanical Exfoliation

In 2004, Geim and Novoselov et al. obtained monolayer graphene using micromechanical exfoliation (i.e., tearing graphite with a tape) and verified the independent existence of 2D crystals. They used an oxygen ion beam to etch 20 m\(^2\) and 5 m deep microgrooves on the surface of a 1 mm-thick highly oriented pyrolytic graphite (HOPG) before pressing it onto a SiO\(_2\)/Si substrate with photoresist. Then, excess graphite flakes were peeled off by repeatedly tearing them with a transparent adhesive tape. Subsequently, the SiO\(_2\)/Si substrate with the remaining adhered micro-flakes was immersed in acetone solution. It was also
sonicated to remove the residual adhesive and most of the thick flake layers from the sample surface. The flake layers, less than 10 nm thick, adsorbed on the SiO₂/Si wafers mainly because of van der Waals forces. Finally, monolayer graphene flakes were selected through optical microscopy and atomic force microscopy (AFM). Although high-quality graphene can be obtained using the exfoliation method, the flake size of these materials is extremely small (only a few tens or hundreds of micrometers). Moreover, the preparation process is difficult to control, and the yield is low, rendering the technique unsuitable for large-scale production and application.

In addition to using tapes to repeatedly tear and pull to obtain graphene, researchers have also exfoliated graphene from graphite sheets using AFM. By fine-tuning the normal stress and scanning speed of the cantilever, the graphite on the substrate can be cut to a thickness of 10–100 nm, and even a single atomic layer of graphene.

Another mechanical exfoliation method for deriving monolayer or multilayer graphene is by sonicating graphite or expanded graphite in solutions (i.e., N-methyl-pyrrolidone, o-dichlorobenzene, and dichlorobenzene). When the surface energy of the solvent in these solutions matches the surface energy of graphene, the interaction between the solvent and graphene can achieve balance, satisfying the energy necessary to exfoliate graphene. The surface tension of the solvent that can exfoliate graphene ranges from 40 mJ/m² to 50 mJ/m². To increase the stability of the graphene solution, researchers have added stabilizers
(SDBS: dodecylbenzene sodium sulfonate, sodium citrate, and other water-soluble substances containing large aromatic rings) during sonication.\textsuperscript{66-67} This prevents graphene agglomeration due to the van der Waals forces among the lamellae. Liquid-phase ultrasonic exfoliation yields multilayers of graphene; however, the yield is low, and obtaining single-layer graphene is difficult.

The initial method for fabricating graphene is mechanical exfoliation. Researchers have conducted numerous studies using samples obtained by this method to determine the undulations of graphene surfaces and measure many physical properties, such as electrical, optical, and thermal characteristics.\textsuperscript{6,59,68-70} This method has been the main technique for obtaining high-quality graphene in the laboratory. However, this approach can only be used for experimental studies; it is unable to satisfy the demand of industrial production because its large-scale application is difficult.

1.2.2 Epitaxial Growth

In the same year (i.e., 2004), at the Georgia Institute of Technology, de Heer et al. epitaxially grew graphene on a single-crystal SiC (0001) surface by heating single-crystal 6H-SiC to remove Si.\textsuperscript{71} The specific procedure is as follows: the SiC obtained by oxygen or hydrogen etching is heated by electron bombardment in vacuum to remove the oxide. After completely removing the oxide from the surface, the temperature of the sample was increased in the range 1250–1450 °C and maintained for 1–20 min to form an extremely thin graphite layer.
Berger et al. successfully employed this method to control the preparation of monolayer or multilayer graphene.\textsuperscript{71} The epitaxial growth method compared with micromechanical exfoliation can be used to prepare large-size and high-quality graphene; this is a crucial step in the development of graphene devices for practical applications. However, the thickness of graphene is determined by the heating temperature, and the preparation of single-thickness samples on a large area is difficult. Moreover, the use of SiC to transfer the obtained graphene to other substrates is extremely expensive.

\subsection*{1.2.3 Oxidation-Reduction Method}

In 2006, Ruoff et al. proposed a chemical method for preparing graphene oxide-based compounds. The technique, also known as the oxidation–reduction method,\textsuperscript{72} is centered on the formation of monolayer graphene oxide by exfoliating graphite oxide. Graphite oxide is formed by the hydrolysis of graphite in the presence of strong oxidizing agents, such as $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, $\text{HClO}_4$, or electrochemical peroxidation. Graphite oxide is also a layered covalent compound, and the distance among layers, approximately 0.8 nm (0.335 nm for graphite), depends on the preparation method. Graphite oxide is generally believed to contain groups, such as $\text{-C}–\text{OH}$, $\text{-C}–\text{O}–\text{C}$, and $\text{-COOH}$.

Different from graphite, the graphite oxide flake layer has strong hydrophilic or polar solvent properties owing to the presence of polar groups. Therefore, graphite
oxide can be exfoliated in water or other polar solvents under the action of external forces (e.g., ultrasonic force) to form a single graphene oxide layer. The resulting graphene oxide is deoxidized and re-graphitized by chemical reduction to restore some of its electrical conductivity while maintaining its geometry. Its electrical conductivity is only partially restored during the redox process, which destroys the high electron mobility of graphene itself. Nevertheless, the process is relatively simple, and the resulting graphene oxide has a high powder-specific surface area (>700 m²/g).

1.2.4 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is an effective method for the large-scale and reproducible preparation of high-quality graphene with a regular structure as well as controlled thickness and size. This method mainly uses transition metals as substrates and forms graphene films on metal surfaces by high-temperature decomposition of carbon compounds (e.g., methane and ethylene). Then, graphene is separated by removing the metal substrate through chemical etching. In 2009, Ruoff et al. was the first to successfully prepare large-area high-quality graphene on Cu foil substrates under similar reaction conditions and obtain graphene with a monolayer structure. CVD growth is the most common approach for producing large-area graphene. However, the produced graphene typically contains defects and small single-crystal grain sizes, which directly affect the electron mobility of graphene. The electronic structure of graphene is closely
related to its layer thickness and interlayer symmetry. The effective preparation of
nanographene and micrometer-sized up to centimeter-sized graphene has already
been achieved. However, improving the quality of CVD-grown graphene crystals
or preparing large-area single-crystal graphene and multilayer graphene with a
certain number of layers is a complex research problem.

1.3 Property and Application

As an ideal 2D crystalline material, graphene exhibits several remarkable physical
properties. Among these, the most frequently studied is electrical property, which
is the most unique graphene property. Charge carriers in graphene can move at
approximately the speed of light; thus, graphene has an extremely high charge
mobility. At room temperature, the carrier mobility of undoped semiconductor
materials can reach 77 000 cm²·V⁻¹·s⁻¹.¹⁷,⁹³⁻¹⁰²

Compared with other materials, graphene has the highest mechanical strength and
thermal conductivity observed thus far.⁷⁰,¹⁰³ The fracture strength of graphene is
as high as 40 N/m, which is a hundred times higher than that of steel. Its hardness
considerably exceeds that of the best diamonds, and its Young's modulus is
approximately 1 TPa. Graphene can be arbitrarily bent, folded, or even curled
without destabilizing its structure. This characteristic is favorable for the
preparation of flexible electrodes. The thermal conductivity of graphene obtained
by micromechanical exfoliation is as high as 5000 W/m·K at room temperature.⁷⁰
That of graphene grown by CVD in a suspension can reach approximately 2500
W/m·K, this property is expected to be applied to the cooling and heat dissipation of chips and microelectromechanical systems.

Graphene exhibits excellent optical properties. For example, monolayer graphene is a zero-bandgap material. Moreover, theoretical calculations and experimental results show that its absorbance is approximately 2.3 %, which is excellent for preparing transparent electrodes.

Owing to the unique electronic, mechanical, and thermal transport properties of graphene, various possible practical applications have emerged. In electronics, graphene exhibits considerable advantages in fabricating transistor channel materials because of its ultrahigh carrier mobility. In addition, graphene can replace the metal wire connection between computer chips and other electronic components, thus reducing resistance and heat generation. In flat panel displays, graphene is expected to replace the depleting indium tin oxide as a transparent conducting electrode.

In the energy field, graphene, with its high electrical conductivity and specific surface area, can also be used as an active substance and anode material in supercapacitors and batteries. Supercapacitors made of graphene have been reported to be twice as high as activated carbon in terms of energy storage density. As an electrode material, graphene can reduce the charging time of lithium batteries to 10 min. Graphene can also be utilized as transparent conductive electrodes in polymer solar cells.
In biology, researchers have attached fluorescent molecules to deoxyribonucleic acid (DNA) to track their reaction with graphene. They found that the fluorescence fade for single-stranded DNA was evident, whereas that for double-stranded DNA was slightly dim. This suggests that single-stranded DNA reacts more strongly with graphene than double-stranded DNA. This unique interaction can be used to construct DNA–graphene biosensors with high sensitivity, selectivity, and biostability.

In the field of chemistry, graphene powder is considered as an excellent filler for composite materials because it improves mechanical properties as well as the electromagnetic shielding effect and heat dissipation. Graphene field-effect transistors can also be used as gas sensors. Furthermore, the properties of graphene can be leveraged for paper materials, conductive inks, catalysts, and transmission electron microscope accessories.

1.4 Overview of Dissertation

This dissertation presents a comprehensive study of the techniques for growing 2D materials by CVD. The growth of large-area high-quality 2D materials was achieved as a result of an in-depth study of the underlying physical mechanisms of CVD. In addition, large-area single-crystal graphene was grown on insulating substrates using a novel growth strategy. A systematic and in-depth study of Cu-based and insulating substrate-based CVD-grown graphene is presented. This
chapter provides a brief overview of the background and development of graphene, hBN, and other 2D materials, including their preparation, properties, and applications.

The materials covered by each chapter are as follows. Chapter 2 systematically introduces the substrates for CVD-synthesized growth, growth process, and transfer techniques for 2D materials. Chapter 3 elaborates on the control of the single-crystal shape and lattice quality of CVD-grown 2D materials using fractal theory. Chapter 4 describes the preparation of single-crystal Cu (111) by long-term high-temperature hydrogen environment annealing employing lattice matching between Cu (111) and Al₂O₃ (0001). Chapter 5 presents the direct growth of large-area single-crystal monolayer graphene on insulating substrates utilizing a single-crystal Cu (111)/sapphire substrate via a specially designed multi-cycle plasma-etching-assisted CVD (MPE-CVD) method. The results of this study are summarized, and future research directions for growing 2D materials are proposed in Chapter 6.
2.1 Growth Substrate Preparations

2.1.1 Conventional Cu Pockets

In the CVD process, the inner surface of the Cu pocket is typically used as a substrate for graphene growth, as shown in Figure 2.1. This is because the evaporation rate of this surface is significantly lower than that of the outer surface for the following reasons. The Cu atoms evaporated at high temperatures collide with the CH₄ and H₂ molecules and unevaporated Cu foil. The Cu atoms that evaporate from the outer surface have a wide space for diffusion. In contrast, those evaporating from the inner surface are partially redeposited on the Cu foil under the dynamic balance of the two collision mechanisms. Therefore, the roughness of the inner surface is significantly less than that of the outer surface. Moreover, the nucleation rate and density of graphene on the inner surface are lower than those on the outside surface, leading to the formation of larger graphene islands and generally flatter graphene samples.

The specific substrate preparation process is as follows.

(1) A solution of ammonium persulfate (NH₄)₂S₂O₈ was prepared. Subsequently, 6 g of ammonium persulfate powder was dissolved in 200 mL of deionized (DI) water, stirred well, and then left to stand.
(2) The Cu surface is cleaned. The Cu foil was cut and dipped into the \((\text{NH}_4)_2\text{S}_2\text{O}_8\) solution for 5 min. This step aimed to remove Cu oxides and other impurities from the Cu surface to obtain a clean Cu surface.

(3) The soaked Cu foil was removed from the \((\text{NH}_4)_2\text{S}_2\text{O}_8\) solution and then soaked in DI water for 3 min to remove residual \((\text{NH}_4)_2\text{S}_2\text{O}_8\) on the Cu surface. Finally, the solution was soaked in ethanol for 3 min, removed, and dried; this removed the residual water on the Cu surface.

(4) The cleaned Cu is folded into a suitable size of Cu pocket, placed in a quartz boat, and put into a tube furnace.

Figure 2.1 Photograph of Cu pocket used for CVD growth.
2.1.2 Polished Cu Substrates

In addition to cleaning using the \((\text{NH}_4)_2\text{S}_2\text{O}_8\) solution, the Cu foil was electrochemically polished to obtain a flatter surface for the growth of large crystalline domains of graphene.\textsuperscript{115-118} The polishing solution was prepared as follows.

1. Phosphoric acid solution (50 mL), ethanol (10 mL), and isopropanol (10 mL) were poured into a wide-mouth bottle. Then, 100 mL of water was added to dilute the solution, and 1 g of urea was added before the solution was stirred.

2. Two pieces of 25-μm-thick Cu foils (10 × 10 mm and 20 × 20 mm) were employed as anode and cathode, respectively.

3. Voltage in the range 2–5 V was applied between the two poles for 3–10 min.

4. The Cu foil cathode was removed and soaked in DI water for a few minutes before it was immersed in alcohol.

5. The Cu foil was removed from alcohol, wrapped in a box, and placed in a tube furnace to initiate graphene growth.

2.2 Chemical Vapor Deposition Growth

2.2.1 CVD Growth Mechanism
The theory of “catalytic nucleation” of graphene on Cu substrates is relatively mature, and scientists have acquired considerable experience in growing high-quality large-area graphene. However, achieving controllable graphene growth remains a pressing problem. In recent years, an increasing number of researchers have focused on resolving this challenge and attained significant progress.\textsuperscript{74,119-127}

Methane is generally presumed to be a carbon source for graphene growth during CVD growth. Carbon atoms were cleaved by hydrogen catalysis and then deposited on the Cu surface to form graphene films.\textsuperscript{91} The entire reaction process was conducted in vacuum (0.1 Pa) and at a high temperature value (1000 °C). Graphene growth results from a dynamic equilibrium of “growth-etching” competition. This means that the growth is manifested by the deposition of carbon atoms on the Cu surface or by the suspension of bonds attached to the edges of nucleated graphene islands. Etching is manifested by the release of carbon atoms on the Cu surface or unfilled bonds on the edges of graphene islands from Cu–C interaction forces or C–C single bonds at high temperatures. In addition to the high temperature, hydrogen, as a strong reducing agent, may also be responsible for the second process. Vlassiouk et al. summarized the relationship between different hydrogen environments and graphene crystal domain sizes under the same conditions.\textsuperscript{128} Figure 2.2 reveals the etching effect of hydrogen on C–C bonds (low-pressure growth at 1000 °C for 30 min and 1 mTorr for methane). As shown in Figure 2.3, researchers from the Chinese Academy of Sciences etched graphene by controlling the ratio of H\textsubscript{2} to Ar to obtain graphene islands with different fractal
shapes. This further confirms the role of H\textsubscript{2} in etching during graphene growth on Cu substrates by CVD.

**Figure 2.2** Effect of hydrogen ratio on crystal domains.\textsuperscript{128}

**Figure 2.3** Different graphene fractal shapes under different H\textsubscript{2} ratios.\textsuperscript{129}
However, the growth mechanisms of graphene on different substrates differ. In early 2009, Kong et al. at MIT and Hong et al. at Sungkyunkwan University in Korea prepared large-area few-layered graphene (FLG) using SiO$_2$/Si wafers deposited with polycrystalline Ni films as substrates and successfully transferred intact graphene from the substrates.$^{130,131}$ They first vaporized a 400-nm Ni film on a SiO$_2$/Si substrate. Methane decomposed when heated in methane gas at 900–1000 °C, and graphene was deposited on the metal surface by the catalytic effect of the metal film. In the same year, Ruoff et al. were the first to use Cu foil as a catalytic substrate. They successfully prepared large-area high-quality monolayer graphene and popularized the use of CVD for graphene preparation.$^{91}$ The growth mechanisms of graphene on Ni and Cu differ. Ruoff et al. used carbon isotope tracking to reveal that these variations in growth mechanisms are due to the different solubilities of carbon atoms in Ni and Cu foils,$^{132}$ as shown in Figure 2.4. Carbon atoms are more soluble in Ni foils, and their solubility increases with temperature. When the temperature rapidly dropped to room temperature, the solubility of the Ni foil decreased. The dissolved carbon atoms became supersaturated and then precipitated onto the metal surface to form graphene. This is the so-called dissolution bias growth method. In contrast, the carbon solubility of Cu foil is low; hence, in this case, the surface self-limiting growth method is employed. In this technique, carbon precursors, such as methane, are catalytically decomposed on the Cu foil surface to obtain free carbon atoms, which accumulate on the foil surface to form graphene. As the coverage of graphene
increases, the catalytic ability of the Cu foil decreases. When the Cu foil surface is completely covered with graphene, graphene growth stops.

Figure 2.4 Different growth mechanisms of graphene on Ni and Cu foils.\textsuperscript{132}

2.2.2 Process of CVD Growth

The growth process of graphene is considered as an example to describe the growth process of graphene on Cu through the CVD method. A 25-\textmu m-thick Cu foil (99.8 % pure; Alfa Aesar) was chosen as the substrate for the experiment. High-purity CH\textsubscript{4} (99.999 %), H\textsubscript{2} (99.999 %), and Ar (99.999 %) were used as carbon
source, catalytic gas, and auxiliary gas, respectively. The growth sequence of graphene is shown in Figure 2.5; the specific growth process is as follows.

(1) Substrate preparation

The Cu foil was cut to a suitable size, and a Cu pocket was created using the method mentioned above. Then, the foil was placed at the center of the thermostatic zone of a quartz tube furnace. A mechanical pump was operated to remove the residual air inside the tube until the pressure becomes less than ~0.1–0.3 Pa.

(2) Hydrogen annealing

Hydrogen was introduced at a flow rate of 2 sccm under approximately 22-mTorr pressure. Then, the temperature was raised to 1030 °C for 15 min to remove surface oxides and increase the grain size of the Cu substrate.

(3) Growth

The hydrogen flow rate was adjusted to 10 sccm, and CH₄ was introduced at a flow rate of 0.1 sccm with partial pressures of 65 and 9 mTorr for hydrogen and methane, respectively. The foregoing was maintained for 6 h according to the growth requirements.

(4) Cooling

The quartz boat with the substrate was pulled outside the tube furnace immediately after graphene growth occurred and rapidly cooled to room temperature with the
same gas mixture as that used in (3) to ensure that the grown graphene crystals were defect-free.

![Time-evolution diagram of gas flow and temperature for the CVD process.](image)

**Figure 2.5** Time-evolution diagram of gas flow and temperature for the CVD process.

### 2.3 Transfer Techniques

Most devices require graphene to be covered with an insulating substrate; hence, graphene from the Cu foil must be transferred to a suitable substrate to understand the properties of this 2D material.\(^{124,133-142}\) Typically, in designing transfer methods, researchers follow the principle of maximizing the integrity of the graphene lattice.
structure during the transfer process and avoid the introduction of other chemical impurities that can affect its properties.

### 2.3.1 PMMA-Assisted Wet Transfer Method

The wet transfer method is the most commonly used technique in laboratories for transferring graphene\textsuperscript{134,136,143} its schematic is shown in Figure 2.6. The specific process is as follows.

(1) Preparation of (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} solution: Weigh 6 g of (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} in a glass, add 200 mL of DI water, and thoroughly stir the mixture with a glass rod.

(2) Preparation of poly(methyl methacrylate) (PMMA) solution: Weigh 2.3 g of PMMA (MW 350 000) into a wide-mouth flask, add 50 mL of chlorobenzene, and stir continuously in a magnetic stirrer for 3 h to ensure that the PMMA particles are completely dissolved in chlorobenzene, forming a homogeneous PMMA solution. Stirring is performed in a sealed fume hood.

(3) Selection of sample area to be transferred: Remove the graphene/Cu pocket from the quartz tube. Cut the sealed edges of the “pocket” with scissors and carefully open the pocket with forceps. Cut off a small piece of the Cu foil to be transferred.

(4) Spin coating of PMMA: Place the cut sample on a small slide, and seal the slide perimeter with adhesive strips to prevent PMMA from entering the back of the sample. Set the spin coater to rotate at 500 rpm. As it rotates, drop an appropriate
amount of PMMA solution onto the graphene surface. After 10 s, spin the PMMA-covered graphene for 40 s at 4000 rpm. Dry the sample naturally in air for 10 min before removing it from the slide. Finally, cut off the PMMA-covered part of the sample edge fixed with adhesive strips.

(5) Etching: Put the PMMA layer of the sample facing up, and allow it to float in the \((\text{NH}_4)_2\text{S}_2\text{O}_8\) solution prepared in the first step. Rinse the backside of the sample with DI water every 10 min to clean the dissolved Cu foil and graphene on the backside. This precludes graphene on the back side from affecting the transfer quality of graphene on the front side. It also prevents bubbles from being generated because of the different solubilities, which affect the transfer quality. Soak the sample 3 to 4 times in the solution until the Cu foil is completely dissolved.

(6) Graphene pick-up: After the Cu foil has been completely etched (usually undisturbed for half a day to one day), dry the PMMA/graphene with clean Si (coated with a 300-nm-thick SiO\textsubscript{2} oxide layer). Then, dry it in an oven heated to ~100–150 °C for 1 h to ensure that graphene is closely attached to its substrate. After baking, allow it to cool down naturally.

(7) Removal of PMMA: Soak the dried PMMA/graphene in acetone five times within the first hour to ensure that the PMMA is removed to the maximum extent.

(8) Cleaning: After soaking, rinse the sample twice with ethanol and then twice with DI water to remove the residual ethanol. Finally, dry the sample naturally. The sample is ready for use.
Graphene obtained by this method is more complete; however, infrequently, a considerable amount of PMMA remains on the surface, resulting in n-type doping. Therefore, designing a better and more convenient laboratory transfer method is also a problem that must be resolved in the future.

Roll-to-Roll Dry Transfer Method

For commercial applications, the roll-to-roll transfer method is the most promising technique for the continuous transfer of 2D material films. Juang et al. first proposed the method of transferring FLG from a nickel foil substrate to a flexible polyethylene terephthalate (PET) target substrate (Figure 2.7). The method specifically required “hot rolling” ethylene vinyl acetate (EVA)/PET and FLG/nickel foil into PET/EVA/FLG/Ni at 150 °C using a hot roller. The hot-rolled material was then placed in a cold roller at room temperature for the nickel foil to peel off from
the PET/EVA/FLG during the constant-speed rolling process. The EVA layer acts as an adhesive to facilitate the tearing of the 2D material.

Figure 2.7 Schematic of the roll-to-roll method for transferring FLG from Ni foil to EVA/PET substrates.\textsuperscript{144}

In the same year, Bae et al. in Korea also applied the roll-to-roll transfer method to successfully transfer 30 in of graphene onto a target substrate (Figure 2.8).\textsuperscript{145} Although the process still uses a solution to etch the substrate, graphene is transferred to the target substrate by applying the roll-to-roll technique to the polymer/graphene/target substrate, thus devising a commercially available large-area transfer strategy for graphene.

Figure 2.8 Flow chart of roll-to-roll large area transfer method.\textsuperscript{145}
The roll-to-roll transfer method is highly efficient. However, the quality of the transferred 2D material is relatively poor because of its tight bond with the polymer, the presence of many residual contaminants on the surface, and the flexibility of the target substrate is limited.

### 2.3.3 Other Transfer Methods

Yang et al. of Nanjing University proposed an ethanol-assisted transfer method applied to the fabrication of 2D van der Waals heterostructures and suspended microbridge devices for thermal transport testing systems (Figure 2.9). They first predicted the effect of ethanol using molecular dynamics and density functional theory (DFT) models. This means that ethanol molecules can spontaneously intercalate into the 2D and matrix materials, thereby significantly weakening the binding force between the 2D material and substrate. This was also confirmed by liquid-phase AFM experiments. After adding ethanol dropwise, the tungsten needle was controlled using an optical microscope. The microscope is equipped with charge-coupled device for imaging and micromanipulation positioning systems to pick up the MoS$_2$ sample from SiO$_2$/Si and precisely transfer it to another SiO$_2$/Si target. Finally, ethanol volatilization completes the transfer process.

This method completely avoids the contamination of the polymer on the surface of the 2D material and damage to the 2D material due to the etching solution. The
2D material can be accurately transferred to any substrate, including the suspended device. Accurate characterization and measurement can be implemented to further improve the performance of 2D materials on the device. Although this method cannot be applied to large-scale commercial production, it has a broad application scope in laboratory research.

![Figure 2.9 Schematic of ethanol-assisted mechanical transfer method](image-url)

Figure 2.9 Schematic of ethanol-assisted mechanical transfer method.
Chapter 3 Crystal-shaped Control of CVD-Grown 2D Materials

3.1 Introduction of Background

Because of their excellent electrical, optical, mechanical, and thermal properties, 2D materials, such as graphene, hBN, and TMD have attracted the considerable attention of the materials science community. Tuning the shape and quality of 2D materials is crucial because both of these affect the performance of nanodevices. Currently, several methods, such as mechanical exfoliation, liquid-phase exfoliation, and CVD, are available for synthesizing high-quality 2D materials. To date, CVD has been considered as the most efficient method for producing large-scale high-quality 2D materials. Moreover, the method allows controlling the shape of 2D material growth. High-quality and defect-free single-crystal 2D materials are essential for extending the application of Moore's law to the current semiconductor production. However, CVD-grown 2D materials are sensitive to growth conditions. Moreover, the underlying physical mechanisms of the fundamental reactions occurring during CVD growth are still not clearly understood at the atomic level. Therefore, the precise control of the shape and crystal quality of 2D materials remains a considerable problem.

Many researchers have attempted to control the growth of 2D materials by CVD. For example, Wu et al. enabled the rapid growth of large-scale single-crystal monolayer graphene. They locally supplied a carbon source to a small-diameter quartz tube above the desired location on the substrate to control the formation of a material with a single nucleus. Lee et al. grew large-size single-crystal hBN on
liquid gold substrates using the limited solubility of B and N atoms in liquid Au to promote high diffusion of adsorbed atoms on the liquid gold surface at high temperatures.\textsuperscript{154} Zhou et al. substantially reduced the melting point of precursors by adding molten salts to increase the reaction rate, allowing the growth of a large number of 2D TMDs.\textsuperscript{155} However, to control the CVD growth process of 2D materials precisely, the physical mechanisms and factors that affect growth must be clearly understood. Many atomic-level physical mechanisms can affect the shape and quality of 2D materials in CVD processes. In the past, researchers have mainly focused on studying macroscopic growth phenomena and rarely explored the deeper atomic-scale mechanisms using atomic-level physical theories.\textsuperscript{156} Consequently, the precise control of the shape and quality of 2D materials in the CVD growth process remains a matter that must be investigated.

This study experimentally and theoretically shows that fractal growth occurs in CVD-synthesized graphene, hBN, and MoS\textsubscript{2}.\textsuperscript{157} In addition, based on the typical diffusion-limited aggregation (DLA) model of fractal theory, a new 2D DLA model is proposed to simulate the molecular dynamics of carbon atoms in CVD-synthesized growth. Its validity and accuracy are demonstrated by comparing the simulation results with experimental data. Moreover, the 2D DLA model is employed to show that the single-domain net growth rate (SD-NGR) is a determinant of domain shape and crystal quality in CVD-grown 2D materials.

This study shows that dendritic structural patterns are common in the CVD-synthesized growth of various 2D materials. To understand this phenomenon, the
growth mechanism in the framework of fractal theory is investigated.\textsuperscript{158} This theory explained the occurrence of irregular or branched natural structures and self-similar patterns of sound with unfolding symmetry.\textsuperscript{159} However, to the author’s best knowledge, this theory has never been applied to explain the growth mechanism of 2D materials synthesized by CVD. In this study, the existence of fractal growth mechanism in CVD-grown graphene, hBN, and MoS\textsubscript{2} is experimentally and theoretically demonstrated. Based on the classical DLA theory,\textsuperscript{160} a typical model of fractal theory, an unconventional 2D DLA model is developed to accurately describe the microscopic kinetics involved in the CVD growth of 2D materials. Then, the model is validated by showing a perfect agreement between numerical simulation results and CVD experimental data. Furthermore, by analyzing the microscopic mechanism of 2D DLA, the SD-NGR is found to be a determinant of the crystal shape and quality of CVD-grown graphene, hBN, MoS\textsubscript{2}, and other 2D materials. By tuning the SD-NGR during CVD, nanomaterials with various fractal morphologies and crystal qualities were synthesized in a controlled manner.

This study provides new guidelines for material scientists working on improving the performance of nanodevices by precisely tuning the properties of 2D materials. It also opens the possibility of applying 2D materials to industrial semiconductor devices and artificial intelligence nanodevices based on low-dimensional materials.

\textbf{3.2 Experimental Section}
3.2.1 Graphene Growth by CVD

Graphene was synthesized on the inner surface of Cu foil pockets (25 µm, 99.8 %, Alfa Aesar) at the temperature of 1030 °C by CVD using a mixture of H₂ and CH₄. As pretreatment, the Cu foils were (a) dipped into aqueous 0.03-g/mL (NH₄)₂S₂O₈ solution for 6 min, (b) rinsed in DI water to remove residues, and (c) dipped again in ethanol to clean their surfaces. As shown in Figure 3.1, the integrated CVD process consists of three parts. (a) In the heating and annealing process, Cu foils were placed on a quartz boat pushed into the tube chamber. Then, the chamber was depressurized from 105 Pa to 0.8 Pa. Next, the chamber was heated up to 1030 °C by a furnace with H₂ flow. (b) In the growth process, graphene grew on the Cu foil with the inflow of CH₄ and H₂ gas mixture. (c) In the cooling process, the tube chamber was rapidly cooled with the same gas mixture used in (b).

![Figure 3.1 Schematic of CVD systems for graphene synthesis.](image)

3.2.2 CVD Synthesis of hBN on Cu
As shown in Figure 3.2, borane ammonia (97%; Aldrich) is used as a precursor and placed in an Al₂O₃ boat for hBN growth. Borane–ammonia started to dissociate, and the products were carried into a chamber that heated the precursor to 90 °C with H₂ flow. After hBN growth, the heating furnace and lamp were rapidly cooled to room temperature.

![Figure 3.2 Schematic of CVD systems for hBN growth.](image)

### 3.2.3 MoS₂ Growth by CVD Method

A schematic of the CVD system used for MoS₂ synthesis is shown in Figure 3.3. Sulfur and MoO₃ powders were used as precursors for the MoS₂ growth. The MoO₃ powder was placed in an Al₂O₃ boat, and the SiO₂/Si substrate was mounted on top of the boat facing down. A separate boat containing sulfur powder was placed next to the MoO₃ powder. Then, the reaction chamber was heated to the growth temperature in the range 600–800 °C at a ramp rate of 50 °C·min⁻¹. After the MoS₂ growth, the furnace was rapidly cooled to room temperature.
3.2.4 Transfer of 2D Materials onto SiO₂/Si Substrate

(1) Graphene was grown on the pockets of Cu foils. Graphene found in the inner pocket was selected because of its relatively high quality. 

(2) Graphene was coated with PMMA solution (PMMA/graphene/Cu foil), and samples were heated at 120 °C for 20 min. 

(3) The samples were turned upside down and placed on the surface of the (NH₄)₂S₂O₈ solution for 3 h. Subsequently, the Cu foils were removed by electrochemical reaction with an aqueous 0.03 g/mL (NH₄)₂S₂O₈ solution. Residual (NH₄)₂S₂O₈ was eliminated by dipping the graphene/PMMA films into DI water. The samples floating on the surface of the (NH₄)₂S₂O₈ solution were picked up every 6 min, and the amorphous carbon that diffused into Cu during the CVD process was flushed. Then, the samples were returned to the (NH₄)₂S₂O₈ solution. After approximately 3 h, all traces of Cu had been removed. Next, all samples were immersed in DI water to remove residual (NH₄)₂S₂O₈.
(4) The SiO$_2$/Si square sheet (1 cm$^2$) was clamped and dipped in DI water. Then, graphene was spooned from underneath. At this point, graphene was naturally situated on the SiO$_2$ sheet, allowing it to dry for 1 h. This gradual drying enabled the moisture trapped between the SiO$_2$ sheet and graphene to escape such that the moisture escape motion did not cause graphene to rupture. Then, the samples were placed in the oven and baked at 120 °C for 30 min to increase the adherence between graphene and SiO$_2$.

(5) The samples were placed at the bottom of a container filled with acetone. Every 15 min, portion T of the used acetone was replaced with a fresh amount to prevent the contact between the samples and air. After repeating this replacement procedure four times, the container was left for 24 h. This replacement process was performed thrice using alcohol to rinse the sample surfaces. Finally, the samples were placed in the CVD tube chamber depressurized to 0.7 pa and heated to 1000 °C. To remove the residual PMMA, hydrogen was allowed to flow through the chamber at 20 sccm for 30 min. Then, the chamber is cooled to room temperature, and the final graphene product is obtained. The transfer method of hBN is similar to that of graphene.

### 3.2.5 Raman and SEM Characterizations of 2D Materials

The Raman spectra and mapping of graphene and MoS$_2$ were obtained using confocal Raman spectroscopy equipment (WITec Alpha 300R, Ulm, Germany) with 10-mW laser energy power, 448-nm laser wavelength, and 300-nm resolution.
The scanning electron microscopy (SEM) images were obtained using a ZEISS MERLIN instrument.

3.3 Study of 2D-DLA Growth Mechanism

This section first introduces the DLA theory. This theory, presented by Witten Jr. and Sander in 1981, is an idealization of the process in which particles are freely released from the edges of a region, randomly wander due to Brownian motion, and then combine to form aggregates. The normal DLA process can form clusters called Brownian trees, which are a type of fractals as shown in Figure 3.4. However, there are no reports in the literature on the use of the DLA theory to study the physics of 2D material growth, which is a complex and an unclear mechanism. In this study, the normal DLA theory is modified in the context of practical situations, and specific physical processes are applied to the synthesis of graphene in the CVD process. The objective is to explore the microscopic mechanisms of 2D material synthesis with the aid of computer simulations.
Figure 3.4 DLA cluster produced from a Cu sulfate solution in an electrodeposition cell, with (a) simulation findings and (b) actual results. The arrival times of the random walkers are indicated by distinct colors in (a).

As mentioned, the DLA theory cannot be directly applied to graphene synthesis because of the differences in physics principles. Here, the real status of graphene in the CVD process is considered based on the DLA model. Moreover, certain modifications to the principle in the DLA theory are introduced. Several physics principles are added: (1) Sp² structure of graphene; (2) Quasi-three-dimensional (3D) growth; and (3) recrystallization, which prevails in graphene. After comparing and modifying the experimental results gradually, the best theory suitable to the synthesis of graphene in the CVD process is named 2D DLA. The emergence of the 2D DLA theory benefits scientists who conduct an in-depth study not only on the growth but also on the physics principle of 2D nanoscale materials.

In this study, graphene, which can serve as an ideal platform to study the fundamental growth mechanism of 2D materials, is initially selected. First, the
2D DLA model is employed to simulate graphene growth by the CVD process in six consecutive stages, as shown in Figure 3.5. These stages are (i) random release, (ii) condensation nucleation, (iii) docking, (iv) recrystallization, (v) graphene hexagon formation, and (vi) film formation.

The following provides a detailed description of each stage. Initially, reactive carbon atoms are randomly released from the periphery of the effective region, which experimentally corresponds to the Cu substrate (2D and quasi-3D release modes). In the second stage, irregular Brownian motion begins once the carbon atoms are released and settle on the surface. When two or more moving atoms are subjected to mutual interactions at a sufficiently close distance, they combine to form condensation nodules and become quiescent. In the third stage, sub-stable or unstable atoms leave the formed graphene as free atoms under the influence of external energy perturbations; stable atoms remain in their positions. Owing to the minimum energy principle, the departing atoms can find a low-energy state. Thus, the proportion of stable atoms in the graphene lattice gradually increases. In the final stage, the carbon atoms condense into hexagonal graphene that eventually forms a graphene film structure.
The growth, atomic model, and recrystallization of graphene are considered to further optimize this model. Moreover, structures generated by the model are compared with experimental results. In laboratory experiments that employ CVD to synthesize graphene, CH$_4$ decomposes into active carbon atoms on the surface of the substrate under the catalytic effect of metal substrates, such as Cu and Ni. This illustrates that carbon atoms can appear from any location on the substrate surface, not only from the boundary regions. Guided by experiments, the model is modified accordingly, upgrading the 2D-release mode to the quasi-3D-release mode.

Next, the energy, growth, and etching mechanism of graphene are considered. The graphene regrowth process after etching is called recrystallization. During the growth of graphene by CVD at temperatures exceeding 1000 °C, unstable carbon atoms may escape from graphene because of the breakage of C–C bonds under energy perturbation. The escaped carbon atoms combine with hydrogen to form...
CHx, which leaves as gas or participates in the formation of graphene. According to the principle of minimum energy, most atoms tend to aggregate at low energy levels. This stabilizes the lattice structure and considerably reduces internal defects and peripheral states, thus improving the quality of graphene structure.

With the modification, the final modeling experimental results were found to conform with the laboratory experimental results. The modeling results are strongly reflected in the 2D DLA fractal tree-shaped simulation results when atom release is limited to the 2D release mode, as shown in Figure 3.6(a). To verify that the 2D release mode can lead to the formation of fractal-shaped graphene, a specific 2D-release composite structure Cu substrate with a sapphire chip cover is experimentally designed. This substrate structure limits the diffusion of active carbon atoms from the edges of the sapphire chip and not randomly from the covered Cu surface.

With this sapphire–Cu substrate, 10 sccm of CH4 and 20 sccm of H2 were allowed to flow during the CVD-synthesized graphene growth. This culminates in the experimental synthesis of another similar dendritic graphene domain, as shown in Figure 3.6(b). A comparison between the experimental and simulation results showed good agreement. A quasi-3D model was employed to obtain accurate simulations of CVD-synthesized graphene growth. The conventional growth model was used with normal Cu as the substrate for the CVD experiments. To synthesize virtually the same graphene domains by CVD, 10-sccm CH4 and 10-sccm H2 were used. The simulation results in the quasi-3D model also agree well with the
experimental results, as shown in Figure 3.6, (c) and (d), respectively. Further, in the bootstrap term of this model, the production rate of active carbon atoms was reduced by increasing the H₂–CH₄ ratio to 50 sccm:5 sccm. Consequently, high-quality defect-free hexagonal CVD-grown graphene domains are obtained; the foregoing is also in good agreement with the simulation results, as shown in Figure 3.6, (e) and (f).

**Figure 3.6** (a) Results of 2D-DLA simulation in 2D-released mode. (b) SEM image of fractal-tree shaped graphene grown at low H₂–CH₄ ratio with the specific substrate by CVD (scale bar: 10 µm). (c) Result from 2D-DLA simulation with the quasi-3D-released mode. (d) SEM image of typical shape of graphene synthesized by CVD (scale bar: 50 µm). (e) Quasi-hexagonal shape with six-fold symmetric structures obtained by 2D-DLA simulation results after involving the recrystallization. (f) SEM image of perfect hexagonal graphene domain synthesized under high H₂–CH₄ ratio (scale bar: 50 µm).

**3.4 Investigation of SD-NGR Influence**
Guided by the foregoing model and the relative comparison of experimental results on real materials grown by CVD after further in-depth analysis, an important influencing factor, defined as the SD-NGR, was found. First, the energy change relationship during the synthesis of graphene by CVD was analyzed. Methane decomposition catalyzed using a Cu substrate produces free active carbon atoms with high energy. With external energy perturbation, thermal excitation energy provided by high temperature, and chemical energy provided by hydrogen, the carbon atoms in the sub-stable or non-stable state have a high possibility of leaving the graphene lattice. These free carbon atoms can participate in the resynthesis of graphene or form gaseous hydrocarbons that leave the reaction cavity under the action of hydrogen gas.

In the actual CVD synthesis process, modulating this interference energy by controlling the growth temperature or gas mass flow ratio between hydrogen and methane is impossible. The modulation of T interference energy means that the possibility of sub-stable atoms escaping from the lattice can be changed. This further influences the relative intensity of etching and coalescence processes and ultimately determines the SD-NGR value for the recrystallization stage, as shown in Figure 3.7. In the case of low SD-NGR, for example, the quantity of atoms with stable energy states increases if the H₂–CH₄ flux ratio or growth temperature is increased. The grown graphene had a perfect island shape and better lattice structure. In the case of high SD-NGR, graphene formed more defects and irregular island shapes. In other words, tuning the SD-NGR is critical to the lattice quality of synthesized graphene.
Figure 3.7 Schematic and energy diagram of free, single-bond, double-bond, and triple-bond atoms as well as external excitation energy determined by growth temperature and H₂–CH₄ ratio.

Next, a detailed study of the factors influencing the SD-NGR in the experiments is conducted. Based on understanding the principle and analysis of the growth process by CVD, the main effects of gas mass flow ratio, growth temperature, and nucleation density on the SD-NGR were investigated. First, the gas ratio was adjusted to modify the SD-NGR under the same growth temperature and substrate roughness conditions. The experimental results show that when the SD-NGR is large, graphene forms a uniformly distributed petal-like shape, as shown in Figure 3.8(a). By contrast, experiments with small SD-NGR values result in the growth of high-quality hexagonal graphene islands, as shown in Figure 3.8(b). In addition to the gas flow ratio, the growth temperature is another factor that affects the SD-
NGR. To verify this claim, the same gas ratio is maintained, and two different growth temperatures (1000 and 1070 °C) are set for graphene growth by CVD in an experiment.

Characterization was performed at the end of the experiment. The results show that graphene grown at low temperatures has more defect (D) peaks in the Raman spectra than that grown at high temperatures, as shown in Figure 3.8(c). In contrast, perfect and virtually defect-free CVD-grown hexagonal graphene is obtained at high temperatures, as shown in Figure 3.8(d).

In addition to the more evident effects mentioned above, graphene nucleation density was also found to affect the SD-NGR. To experimentally verify this presumption, two sets of control experiments were conducted on substrates with different degrees of roughness, which could cause various nucleation densities. Under the same growth conditions of the gas environment and furnace temperature, the two systems had equal total amounts of active carbon atoms per unit time on the surface of the Cu substrate. Thus, high nucleation density values lead to the low average capture of active carbon atoms per nucleus; this results in smaller SD-NGR values, which improve the quality of graphene formation. Note that most of the formed graphene is hexagonal in shape, as shown in Figure 3.8(e). In contrast, a smooth surface results in low nucleation density. The experimental results on CVD-synthesized growth showed that graphene forms large leaf-shaped islands when the nucleation density was low (Figure 3.8(f)). This leads to the conclusion that tuning the SD-NGR can be achieved by adjusting specific
parameters (temperature, gas flow rate, and substrate) in the growth experiments. Consequently, the quality and lattice shape of grown graphene can be affected.

![Figure 3.8](image.png)

**Figure 3.8** (a) Raman characteristics of star-shaped graphene grown under low H₂–CH₄ ratio (scale bar: 60 µm). (b) Raman mappings and spectra of hexagon-shaped graphene synthesized under high gas rate ratio (scale bar: 20 µm). Raman characteristics of graphene with crystal quality grown at (c) 1000 and (d) 1070 °C (scale bar: 100 µm). (e) Raman mappings and spectra of large leaf-like graphene petals due to low nucleation density (scale bar: 60 µm). (f) Magnified view of small hexagon-shaped graphene due to high nucleation density (scale bar: 20 µm).

### 3.5 Precise Grain Shape Control based on Fractal Theory

Based on the 2D DLA model presented above and influencing factors derived from the analysis of the combined model and actual CVD experimental results, the equivalent SD-NGR effect on the CVD-synthesized graphene growth is extended to other 2D materials, such as hBN and MoS₂. The tuning of actual experimental parameters was guided by the simulations, resulting in different types of fractal single-crystal shapes. The growth conditions for each material are as follows.

First, the CVD-synthesized graphene growth is regulated. As shown in Figure 3.9(a), fractal dendritic graphene islands in sapphire and Cu foil sandwich are
prepared by limiting the gas flow rate ratio to 1:2 with 10 sccm of CH₄ and 20 sccm of H₂. In addition, the conventional clean Cu foil is modified as the growth substrate, and the gas ratio is adjusted to 1:4 with flow values of 5-sccm CH₄ and 20-sccm H₂. After the same CVD-synthesized growth time, sixfold symmetric petal-like graphene islands are observed on the Cu surface, as shown in Figure 3.9(b). Furthermore, to obtain minimal SD-NGR values, the gas ratio during growth was adjusted to 1:12 with flow values of 5 sccm of CH₄ and 60 sccm of H₂. After approximately 50 min of CVD-synthesized growth, the graphene islands exhibit a standard sixfold symmetry of a perfect hexagonal shape, as shown in Figure 3.9(c).

Similar to graphene growth regulation, the hBN growth is also controlled. Specifically, various fractal hBN single crystals are grown by adjusting the gas flow rate ratio of H₂ to Ar (carrier gas) during the hBN synthesis. In real experiments, the 90 °C source zone temperature and sufficient borane ammonia source are maintained. Fractal hBN single crystals with different island shapes were successfully synthesized by CVD by tuning the gas flow rate ratio. Fractal-shaped hBN was grown experimentally by CVD with a gas flow rate of H₂:Ar = 10 sccm:10 sccm, and quasi-hexagonal hBN was grown in the CVD process at flow rates of 10-sccm Ar and 7-sccm H₂. The most stable triangular hBN with triple symmetry is successfully grown using 20 sccm of Ar and 5 sccm of H₂, as shown in Figure 3.9, (d)–(f).
In addition to graphene and hBN, the simulation results and growth theory are applied to TMDs. Among TMD materials, MoS$_2$ has the most representative case of growth. The heating region of the sulfur source is set to 180 °C, and the flow rate of the carrier gas, Ar, is regulated to control growth shape and quality using the SD-NGR; the Ar gas flow rates are 30, 17, and 5 sccm. Finally, after growth, three different domain shapes are obtained, as shown in Figure 3.9: spherical fractal tree, quasi-hexagonal symmetric star, and standard triple-symmetric triangular MoS$_2$ single crystal. These experimental results satisfactorily indicate that the proposed 2D DLA model and SD-NGR regulation theory are applicable to the CVD-synthesized growth of most 2D materials. With the aid of theoretical simulation and study of intrinsic mechanism, the parameters of the growth process by CVD can be reasonably regulated to achieve the controlled synthesis of high-quality large-area 2D materials.
Figure 3.9 SEM images of 2D materials with typical fractal shapes in precisely controlled CVD-synthesized growth. (a) Fractal tree-shaped graphene domain with specific growth substrate structures (scale bar: 10 μm). (b) Petal-shaped graphene grown under low hydrogen–methane gas flow ratio (scale bar: 50 μm). (c) Perfect hexagonal-shaped graphene domains under high H₂–CH₄ ratio (scale bar: 50 μm). (d) Self-similar structures of hBN grown under low H₂–Ar flow ratio (scale bar: 10 μm). (e) Quasi-hexagonal domains under medium H₂–Ar gas flow ratio (scale bar: 20 μm). (f) Regular triangular-shaped hBN grown under high H₂–Ar gas flow ratio (scale bar: 20 μm). (g)–(i) Fractal-shaped MoS₂ domains grown under Ar gas flow rates of 30, 17, and 5 sccm (scale bar: 10 μm).
3.6 Conclusion

As promising advanced materials, 2D materials, such as graphene, hBN, and MoS$_2$, exhibit remarkable physical and chemical properties. Accordingly, they have been widely applied to electrical and optical nanodevices. However, a remaining challenge is for material scientists to synthesize large-scale high-quality single-crystal 2D materials. To resolve this problem, the author endeavored to explore the micro-mechanism of 2D material growth. In this regard, the author noted that an old theory, named DLA (which describes a process in which free particles are released from the edge of systems, randomly walk, cluster together, and grow into materials), has been used in many areas of Physics. Unfortunately, reports in the literature have not mentioned the combined use of DLA theory and 2D materials. This is because the DLA theory cannot be directly applied to 2D materials owing to variations in physics principles.

Based on the normal DLA theory, graphene is selected as a representative 2D material in this research. The study considers the micro mechanism of graphene synthesis in the CVD process. Moreover, the DLA theory is reconsidered by adding several physics principles, as follows. (a) The sp$^2$ hybridization of carbon atoms in graphene is considered; the band angle of C–C must be 120°. (b) The dimension of systems is modified from 2D to quasi-3D because of the special growth mode of graphene in the CVD process. (c) The recrystallization process, which plays a critical role in reducing defects and improving the crystal structure quality of graphene, is considered. By comparing the experimental results obtained by SEM
and Raman microscopy, and by modifying the theory step by step, a theory that best suits the synthesis of graphene in the CVD process is formulated and tentatively named 2D DLA. Communities that are involved in the study of 2D-nanoscale materials not only to grow but also thoroughly understand the physics principles of these materials are anticipated to benefit from the proposed of 2D DLA process.

One innovative concept in this research is to investigate the microphysics mechanism of 2D material synthesis using the proposed 2D DLA model. The SD-NGR is found to be the key to maneuver the shape and crystal quality of 2D materials during CVD-synthesized growth. Accordingly, several different experiments have been conducted to verify the idea, which involves changing the SD-NGR in different ways. As expected, the results of these experiments show a distinct relationship between the SD-NGR and 2D material domain (shape and crystal quality). This verifies that the SD-NGR plays a key role in influencing the crystal quality and shape of 2D materials in CVD-synthesized growth. This study is anticipated to advance the 2D nanomaterial research.
Chapter 4 Producing Single-Crystal Cu from Polycrystalline Cu

4.1 Introduction of Background

Currently, the growth of most 2D materials, such as graphene and hBN, relies on metallic surfaces. In this case, Cu, as the primary metal substrate, is essential.80,87,125,163-165 In recent years, the number of researchers who have endeavored to grow graphene and hBN on single-crystal Cu surfaces has increased.166-177 They demonstrated that single-crystal Cu is a more favorable substrate for synthesizing single-crystal 2D materials. Currently, single-crystal Cu blocks are the primary source of single-crystal Cu. Commercial single-crystal metals are typically synthesized by block-crystal growth or depositing thin films on substrates, which are small and expensive. Actual experiments do not require thick blocks of single-crystal Cu; typical micrometer-sized single-crystal Cu foils are sufficient for growing 2D materials. Therefore, developing a method for synthesizing single-crystal Cu foils is crucial.

The industrial-scale production of single-crystal Cu foils is essential for the industrial growth of 2D materials, such as single-crystal graphene. Polycrystalline metals have grain boundaries. In contrast, single-crystal metals without grain boundaries exhibit better properties. Graphene synthesized on polycrystalline metals increases electron scattering at the grain boundaries, consequently degrading the quality of materials.178,179 Currently, the graphene CVD synthesis on single crystalline metal substrates has attracted considerable interest because of the small lattice mismatch between single-crystal metal foils and graphene. This
means that the lattice mismatch between graphene and Cu (111) is ~3–4 %.\textsuperscript{82,180} Here, Cu (111) can be used as a substrate for single-crystal grain boundary-free uniform graphene epitaxial growth.\textsuperscript{181-185} It can also be utilized for the epitaxial growth of large-area hBN, further increasing the interest in and demand for large-area single-crystal metal substrates.

Recently, by heating foils close to their melting temperature and under hydrogen atmosphere, Ruoff et al. found unusual transitions from polycrystalline grains to specific orientations in the in-plane and normal directions.\textsuperscript{186} This specific orientation may be produced by lattice rotation accompanied by the elimination of stacking layer errors, resulting in a reduction in surface energy. With this “contact-free annealing,” Cu (111), Ni(111), Co(0001), Pt(111), and Pd(111) single-crystal foils with grain sizes of up to 32 cm\textsuperscript{2} were prepared. In addition to the large-scale fabrication of Cu, Ni, Co, Pt, and Pd foils, large areas of single-crystal metal foils can be obtained from other polycrystalline foils using this process. In addition, Liu et al. designed a pre-oxidation treatment approach to manufacture large grain seeds with high index facets using commercial polycrystalline Cu foils.\textsuperscript{187} The Cu foils were oxidized in air for several hours at 150–650 °C before they were annealed in a reducing atmosphere at 1020 °C for several hours to successfully synthesize single-crystal 30 × 20 cm\textsuperscript{2} Cu foils. The technique of Liu et al. also applies to the growth of high-index single-crystal Ni foils. The research of many scientists has led to the increasing possibility of using single-crystal Cu foil as a substrate for the epitaxial growth of 2D materials.
In this study, c-plane sapphire with commercially available polycrystalline Cu foil was used as a substrate. The polycrystalline Cu foil placed on a single-crystal sapphire gradually transformed into a single-crystal Cu (111) foil.\textsuperscript{188} After fading in a high-temperature hydrogen environment, Cu (111) tightly adhered to the sapphire substrate. In addition to the improved experiment preparation, DFT calculations were implemented. This enabled the computation of the stacking energy of various Cu crystalline phases on different Al\textsubscript{2}O\textsubscript{3} crystalline phases to support the experimental results from a theoretical perspective. In addition, the prepared single-crystal Cu foils were characterized using optical microscopy, SEM, electron backscatter diffraction (EBSD)–inverse pole figure (IPF), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), and other techniques.

4.2 Experimental Section

4.2.1 High-temperature Annealing

This section describes the technical details of preparing single-crystal Cu films on Al\textsubscript{2}O\textsubscript{3} (0001). The polishing solution was a mixture of H\textsubscript{3}PO\textsubscript{4}, ethanol, isopropanol, DI water, and urea. Commercial polycrystalline Cu foil (25-μm thick, 99.9 % pure; Nilaco Co.) was electrochemically polished by connecting the foil to a voltage source meter in the polishing solution. After polishing, the Cu foil was soaked in acetone, isopropyl alcohol, and DI water for cleaning (5 min in each solvent). The
samples were removed, dried, and set aside. Next, the acid etching solution for the sapphire substrate was first prepared using a 1:3 H₂SO₄–H₃PO₄ ratio. The washed sapphire wafer sample was placed in an etching solution preheated to 300 °C for 25 min. After etching, the sample was removed and cleaned again with DI water; the surface was cleaned with oxygen plasma. Next, the polished Cu foil was flattened using a conventional laminator. It was subsequently protected on both sides with a PET film, which was removed and placed on the surface of a clean Al₂O₃ (0001) substrate. The Cu foil was observed to adhere well to the surface spontaneously. Then, the Cu/Al₂O₃ (0001) sample was placed in a quartz boat and inserted into a CVD-system quartz tube. The samples were heated to 1350 K in H₂ (99.999 %, liquefied air) and Ar (99.999 %, liquefied air) atmospheres with flow rates of 50 and 50 sccm, respectively, and 750-Torr pressure for 24–30 h. The total annealing time slightly varied depending on the lateral dimensions of the Cu film attached to Al₂O₃ (0001). During this long annealing process, the polycrystalline Cu foil gradually transformed into a single-crystal Cu (111) film. Then, the system was cooled from 1350 to 373 K at an average cooling rate of 80 K/min and from 373 K to room temperature at 10 K/min. After annealing, the samples were removed, and the Cu (111) films were observed to firmly adhere to the Al₂O₃ (0001) substrate.

4.2.2 AFM, EBSD, and XRD Characterization
In this study, we used an EBSD attachment (Oxford Instruments) in SEM (Quanta 600, FEI) to characterize the grain structure of Cu foils and films on Al₂O₃ (0001). The surface morphologies of the single and polycrystalline Cu were then characterized using AFM (Dimension Icon, Bruker). Furthermore, XRD (D2 PHASER, Bruker) was used to test the Cu foil and Al₂O₃ (0001) in the single-crystal or polycrystalline state (Figure 4.1).

**Figure 4.1** XRD characterization of non-annealed polycrystalline Cu and single-crystal Cu (111). (a) Photograph of non-annealed polycrystalline Cu foil on Al₂O₃ (0001) substrate. (b) XRD spectra of polycrystalline Cu foil shown in (a). The Cu (111), Cu (200), and Cu (220) peak are distinctly observed in the spectra. (c) Photograph of annealed polycrystalline Cu (111) foil on Al₂O₃ (0001) substrate (annealing time: 30 h). (d) XRD spectra of annealed Cu (111) foil shown in (c). Only the sharp Cu (111) peak and the substrate peak are observed in the spectra.
4.2.3 HR-TEM and HAADF–STEM Characterization

Cross-sections of specimens for transmission electron microscopy (TEM) were prepared using a focused ion beam (FIB; Helios 400S, FEI). To protect the sample from ion beam damage, it was passivated using electron beam-assisted Pt (300 nm) before exposure. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging, HR-TEM imaging, and energy dispersive microscopy (EDS) mapping were performed using TEM (Titan Themis Z, FEI). The TEM instrument is equipped with a high-brightness electron gun (x-FEG), an electron beam monochromator, and a double Cs corrector operated at 300 kV.

4.2.4 DFT Calculation

By the DFT, the growth of Cu layers on Al-terminated and O-terminated Al₂O₃ (0001) surfaces was calculated. The single-crystal Cu (111) surface was found to be the only stable contact with the Al₂O₃ (0001) surface. The interactions between Al₂O₃ (0001) and Cu (111) were covalent. Graphene deposited on the Al₂O₃ (0001) and Cu (111) surfaces has a single-crystalline structure and forms van der Waals contacts. Moreover, Cu (111) on Al₂O₃ (0001) at the graphene-capped end is a single crystal. Because of their significant lattice mismatch, determining the contacts of Cu (1010) and Cu (1120) with Al₂O₃ is computationally impossible. All simulations were implemented by the Vienna ab initio simulation package using the projector augmented-wave method and the Perdew–Burke–Ernzerhof form of
the generalized gradient approximation for the electron exchange correlation potential. The Grimme method was used for the van der Waals correction.

For the plane wave expansion, the selected cutoff energy was 500 eV. The force criterion for structural relaxation was set to 0.001 eV/Å; a $7 \times 7 \times 1$ k-mesh was used. To minimize the lattice mismatch among the components, $2 \times 2 \times 1$ Cu (111) and graphene supercells were combined with a unit cell of Al$_2$O$_3$ (0001). A 14.67-Å-thick nine-layer slab of Cu (111) was used (five layers fixed to the bulk structure and four layers free to relax). An 11.15-Å-thick O-terminated or 10.15-Å-thick Al-terminated five-layer slab of Al$_2$O$_3$ (0001) was added (three layers fixed to the bulk structure and two layers free to relax). The slab model was completed using a 20-Å-thick vacuum layer. All calculations were performed at 0 K.

### 4.2.5 Transfer of Conventionally Grown Graphene

Conventionally grown graphene was spin-coated for 1 min using PMMA (i.e., 950 PMMA C4) and then heated at 120 °C for 20 min. Next, the Cu foil was etched using a 0.03-g/mL (NH$_4$)$_2$S$_2$O$_8$ solution. An arbitrary substrate was employed to hold the PMMA/graphene material; it was dried in air for 1 h. Then, the samples were baked in an oven at 120 °C for 30 min. Finally, acetone was used to remove the PMMA.
4.3 Fabrication Process of Single-Crystal Cu Film

Recent studies have shown that the structure and properties of metal substrates significantly affect the crystal orientation and domain symmetry of materials. Accordingly, considerable effort has been devoted to the preparation of metal substrates to improve the quality of 2D materials.\textsuperscript{133} Currently, Cu (111) is considered to be an ideal substrate for synthesizing single-crystal graphene 2D materials with triangular hBN and hexagonal symmetry.\textsuperscript{189,190} Hence, the preparation of large single-crystal Cu foils is crucial for synthesizing high-quality wafer-scale 2D materials. In a previous study, single-crystal Cu (111) foils were fabricated via contactless annealing.\textsuperscript{186} Inspired by the aforementioned, the current study successfully produced 2-in single-crystal Cu (111) foils on \textit{Al}_2\textit{O}_3 (0001) substrates by long-term near-melting temperature annealing in a hydrogen–argon atmosphere using the lattice matching of single-crystal Cu (111) and \textit{Al}_2\textit{O}_3. A schematic of the fabrication process for single-crystal Cu (111) is shown in Figure 4.2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fabrication_process}
\caption{Schematic of fabrication process of single-crystal Cu (111) foil from commercial polycrystalline Cu foil on \textit{Al}_2\textit{O}_3 (0001).}
\end{figure}
This section describes the experimental procedure. First, the purchased polycrystalline Cu foil was electrochemically polished using a polishing solution. The Al₂O₃ (0001) substrate was etched using an acid solution, cleaned, and then surface-cleaned using O plasma. The polished polycrystalline Cu foil was then laminated onto an O₂ plasma-treated Al₂O₃ (0001) substrate. The Cu foil spontaneously and tightly adhered to the Al₂O₃ (0001) surface, forming a Cu/Al₂O₃ van der Waals heterostructure, which was placed in a CVD system. The tube furnace was heated to 1075 °C, and the pressure was controlled at 750 Torr while 50-sccm H₂ and 50-sccm Ar were introduced. The heterostructure was annealed under these conditions for 30 h. According to the energy distribution calculated by the DFT (described in the following sections), Cu (111) is the most stable crystal on the Al₂O₃ (0001) substrate and has the lowest steady-state stacking energy compared with the Cu (110) and Cu (100) crystals, as The energy diagram is shown in Figure 4.3.
Figure 4.3 Energy diagram of Cu (110), Cu (100), and Cu (111) crystals on an Al₂O₃ (0001) surface.

During the annealing process, crystals with different orientations gradually relax and transform into Cu (111) with the lowest stacking energy. They form single crystals to reduce the grain boundary energy under thermal energy perturbation near the melting temperature. A schematic of the transformation process is shown in Figure 4.4. Single-crystal Cu (111) was successfully prepared on an Al₂O₃ (0001) substrate. This substrate can be used for growing large-area single-crystal graphene and hBN.

Figure 4.4 Schematic of transformation process from commercial polycrystalline Cu foil into single-crystal Cu (111) film on Al₂O₃ (0001).

4.4 Transformation Mechanism and Stacking Energy Calculation
To theoretically investigate and calculate the feasibility of graphene crystalline phase transformation of Cu (111) at the Al$_2$O$_3$ interface, the underlying physical mechanisms observed experimentally were examined based on DFT simulations.

For the DFT simulation, nine models using the Cu (110), Cu (100), Cu (111), Al$_2$O$_3$ (11-20), Al$_2$O$_3$(10-10), and Al$_2$O$_3$ (0001) surfaces were constructed. The combined models are listed as Cu (110)–Al$_2$O$_3$ (11-20), Cu (100)–Al$_2$O$_3$ (11-20), Cu (111)–Al$_2$O$_3$ (11-20), Cu (110)–Al$_2$O$_3$ (10-10), Cu (100)–Al$_2$O$_3$ (10-10), Cu (111)–Al$_2$O$_3$ (10-10), Cu (110)–Al$_2$O$_3$ (0001), Cu (100)–Al$_2$O$_3$ (0001), and Cu (111)–Al$_2$O$_3$ (0001). As shown in Figure 4.5, the crystal symmetry and lattice mismatch of the nine models are investigated. Among them, the combination of Cu (111) and Al$_2$O$_3$ (0001) exhibited hexagonal symmetry and the best lattice coherence compared with the other models; its minimum lattice mismatch is 6.5 %. The calculated stacking energies of 0.98, 1.33, and 2.09 eV per Cu atom for Cu (110), Cu (100), and Cu (111) on Al$_2$O$_3$ (0001), respectively, indicate that Cu (111) stacked on Al$_2$O$_3$ (0001) is favorable, as shown in Figure 4.6.
Figure 4.5 Atomic structures and DFT simulations of Cu on Al₂O₃ after relaxation. 
(a) Top and side views of atomic structures of Cu(110), Cu(100), and Cu (111) on 
Al₂O₃ (0001) after relaxation. (b) Stacking energies of Cu(100), Cu(110), and Cu 
(111) on Al₂O₃ (0001). (c) Top and side views of atomic structures of Cu(110), 
Cu(100), and Cu (111) on Al₂O₃(10-10) after relaxation. (d) Stacking energies of 
Cu(100), Cu(110), and Cu (111) on Al₂O₃(10-10). (e) Top and side views of atomic 
structures of Cu(110), Cu(100), and Cu (111) on Al₂O₃(11-20) after relaxation. (f) 
Stacking energies of Cu(100), Cu(110), and Cu (111) on Al₂O₃(11-20). Cu, Al, and 
O atoms are shown in gold, blue, and red color, respectively.
Figure 4.6 (a) Atomic structures of Cu on Al$_2$O$_3$ (0001) after relaxation. Top view from <0001> direction and side view from <11-20> direction. Cu, Al, and O atoms are shown in gold, blue, and red, respectively. (b) Stacking energies of Cu (100), Cu (110), and Cu (111) on Al$_2$O$_3$ (0001).

Subsequently, the interaction between the Cu foil and Al$_2$O$_3$ substrate was further investigated by simulating both O-terminated and Al-terminated Al$_2$O$_3$ (0001) substrates. The stacking energy of each Cu atom on the O-terminal Al$_2$O$_3$ (0001) substrate is 2.09 eV. This is lower than the 1.04-eV stacking energy of each Cu atom on the Al-terminal Al$_2$O$_3$ (0001), as shown in Figure 4.7. The figure indicates that the higher energy states of Cu (110) and Cu (100) caused by the larger lattice mismatch lead to a gradual conversion to Cu (111) as the temperature approaches the melting temperature. This theoretically explains the transformation of polycrystalline to single-crystal Cu on Al$_2$O$_3$ (0001) substrates during high-temperature annealing.
4.5 Wafer-Scale Cu (111) Formation and Characterization

Polycrystalline Cu was successfully converted into single-crystal Cu (111) on a sapphire (0001) substrate using the high-temperature annealing method described above. Then, the prepared single-crystalline Cu foils were further characterized. To study the variation of the Cu crystalline phase with annealing time, Cu foil annealing experiments were performed at different periods. The annealing times for each group of experiments were set as 5, 10, 15, 20, and 25 h to perform a series of related experiments. After conducting the experiments, data from 10 samples measured in each set of experiments showed that the grain size of Cu
(111) crystals gradually increased with the annealing time. Eventually, the entire 100-mm² Al₂O₃ (0001) substrate is covered, as shown in Figure 4.8.

Figure 4.8 Photograph of Cu foil (10 × 10 mm²) annealed at different times (5–25 h). Largest Cu grain of each sample is indicated by dashed circle; corresponding Cu grain size distributions obtained by measuring 10 samples for each annealing time are also shown.

Because Cu foil crystalline phases are not easily observed under an optical microscope, the prepared Cu foil is heated on a heating stage in air to oxidize the Cu surface. Because the color of Cu oxide (CuOₓ) varies according to its crystalline orientation, the phase transition can be easily observed in the optical image of the oxidized Cu foil sample, as shown in Figure 4.9. As the annealing time increased, the number of Cu crystalline phases gradually decreased within the field of view. The grain size gradually increased, eventually merging into a single crystalline phase.
Figure 4.9 Optical micrograph of Cu foil surface (10 × 10 mm² after oxidization treatment) along various annealing times. (a)–(i) Samples of different annealing times from 0 to 25 h. Number of Cu grains gradually decreases, and size of largest grain increases until entire area is filled.

In addition, to determine whether crystalline phase transitions occur in polycrystalline Cu with different substrate materials or crystalline phases of the
same substrate material, the same annealing experiments are performed using various substrates, such as quartz, Al₂O₃ (10-10), and Al₂O₃ (11-20). Based on the experimental results, no polycrystalline Cu exhibits a transition to single-crystal Cu (111) crystals on these substrates, as shown in Figure 4.10.

**Figure 4.10** Photograph of Cu foil surface (10 × 10 mm²) with various substrates. (a) Quartz, (b) Al₂O₃ (10-10), (c) Al₂O₃ (11-20), and (d) Al₂O₃ (0001). Corresponding Cu grain size distributions from 10 samples at each annealing time.

Phase transformation and single crystallization can be achieved for Cu foils of any size under high-temperature annealing because of spatial homogeneity. The size of the resulting single-crystal Cu is limited only by the size of the sapphire substrate and CVD constant-temperature zone. Accordingly, 2-in single-crystalline Cu (111) foils were prepared on Al₂O₃ (0001) using a larger sapphire substrate and more extensive CVD apparatus by adjusting the annealing conditions and extending the annealing time. The surface of the prepared 2-in Cu single crystal was observed
using an optical microscope. The Cu (111) single crystal virtually covers the entire area without any distinct grain boundaries, as shown in Figure 4.11(a) and Figure 4.12.

In addition, the crystal orientation of the fabricated Cu (111) foil is confirmed using SEM and EBSD. The IPF map based on the Cu (111) texture does not exhibit any contrasting difference across the entire area, as shown in Figure 4.11(b). Moreover, XRD analysis verifies the crystalline phase and quality of the fabricated single-crystal Cu (111) foils. The XRD spectra exhibit highly consistent sharp Cu (111) peaks with high signal-to-noise ratios, as shown in Figure 4.11(c).

**Figure 4.11** (a) Optical micrograph of fabricated 2-in single-crystal Cu (111) foil; area is divided into nine parts for further characterization. (b) EBSD IPF maps of nine areas in (a). (c) XRD spectra of marked areas in (a). (d) Cross-sectional HR-TEM image of Cu (111)/Al₂O₃ (0001) interface.
**Figure 4.12** Photograph of produced large-scale Cu foil after oxidization treatment. (a)–(d) Photograph of 2-in oxidized Cu foil at various annealing times from 5 h to 30 h. Color contrast indicates different crystal grains. (e) Cu foil annealed for 5 h on 4-in Al₂O₃ (0001) wafer; each crystal grain is clearly observed. (f) Cu foil annealed for 35 h on 4-in Al₂O₃ (0001) wafer; Cu (111) crystal virtually occupies entire area at 72 mm.

During the Cu (111)/Al₂O₃ (0001) heterostructure annealing, the Cu foil gradually adheres tightly to the upper surface of Al₂O₃ (0001), resulting in a significantly lower gap between Cu (111) and Al₂O₃ (0001). A cross-sectional sample is prepared using FIB to further observe the interfacial state of the formed Cu (111)/Al₂O₃ (0001) heterostructure at the atomic-level resolution using HR-TEM,
as shown in Figure 4.11(d). As depicted in Figure 4.13, the distance between Cu (111) and Al₂O₃ (0001) is approximately 2.15 Å, as measured by the cross-sectional HR-TEM and HAADF-STEM. Single-crystal diffraction spots of Cu (111) and Al₂O₃ were obtained using selected area electron diffraction (SAED); the spots showed satisfactory lattice match.

**Figure 4.13** Electron microscopy and EDS of region of Cu (111)/Al₂O₃ (0001) interface. (a)–(b) Intensity profiles along red and blue lines. (c) High-resolution cross-sectional transmission electron image of Cu (111)/Al₂O₃ (0001) interface. (d) SAED pattern obtained from Cu region in (c). (e) SAED pattern obtained from Al₂O₃ region in (c). (f) Cross-sectional HAADF-STEM image of Cu (111)/Al₂O₃ (0001) interface in region marked in (c). (g) Corresponding EDS elemental mapping of Cu (111)/Al₂O₃ (0001) interface.
Furthermore, considering that the two single crystals fully adhered to each other, the surface of Cu and sapphire were tested using AFM. The analysis revealed a flat bottom interface surface of the long-term annealed Cu (111) surface that was smoother than its top surface. The results show that the long-term annealed Cu (111) bottom surface is smooth with a 6-nm roughness value. This is significantly lower than that of the Cu (111) top surface but approximately equal to that of the Al$_2$O$_3$ (0001) surface, as shown in Figure 4.14.

**Figure 4.14** Surface roughness measurements of Cu foil. AFM characterizations of (a) top surface of Cu foil, (b) bottom surface of Cu foil, and (c) surface of Al$_2$O$_3$ (0001) substrate after long-term annealing process. Height profile figures are all set to y-axis for comparison. (d)–(f) Photographs of annealed Cu/Al$_2$O$_3$ (0001) sample. Top surface is rough, and bottom surface is smooth. In (f), mirror-like surface is observed from backside of Al$_2$O$_3$ (0001) substrate.
4.6 Conclusion

In recent years, the discovery of new physical properties of graphene has generated renewed interest in the scientific community. However, the quality of graphene is limited by the current synthesis techniques. The widely used CVD method is typically applied with a Cu foil as substrate. Consequently, the preparation of large-scale single-crystal Cu foils is currently attracting considerable attention from scientists because of its importance in the growth of 2D materials. Accordingly, devising a method to prepare single-crystal Cu (111) foils is important to the growth of single-crystal graphene.

This study exploited the excellent lattice match between single-crystal Cu (111) and single-crystal Al$_2$O$_3$ (0001), which have the same crystal symmetry. The stacking energy of Cu atoms on sapphire (0001) was calculated by DFT. The production of wafer-sized micrometer-thick single-crystal Cu (111) foils was achieved on 2-in substrates using high-temperature annealing in hydrogen atmosphere (i.e., the transformation of commercially purchased polycrystalline Cu foils to single-crystalline Cu foils). The prepared single-crystal Cu (111) surface was examined using optical microscopy and SEM. The surface was uniform and had no visible grain boundaries. The crystalline phase of the prepared single-crystal Cu foils was further determined using XRD and EBSD. The top and bottom surface roughness values of the prepared single-crystalline Cu and roughness of the sapphire substrate were examined using AFM. Finally, interfacial samples were obtained using FIB. Images with atomic-level resolution were obtained using
HR-TEM. Single-crystal diffraction spots of Cu (111) and Al₂O₃ were obtained using SAED.

The single-crystal metal foils prepared in this study can be applied to 2D material growth research, surface science, catalytic research, thermally conductive material applications, and various other applications. Hence, metal foils are necessary for the industrial synthesis of large-area 2D materials in the future.
Chapter 5 Single-Crystal Graphene Grown on Insulators

5.1 Introduction of Background

As the first 2D nanomaterial, graphene has attracted considerable attention from the scientific community. Due to its excellent physicochemical properties, the application of graphene is expected to lead to technological breakthroughs in next-generation semiconductor nanodevices. However, the expected value and theoretically predicted properties of graphene have not yet been realized because of the limitations of graphene synthesis technology. Currently, CVD is the most widely used synthetic method for growing large high-quality graphene. However, conventional Cu-substrate CVD-grown graphene inevitably suffers from electron scattering at grain boundaries, folds, and adlayers. This severely affects its electronic properties of graphene, consequently limiting its application in the semiconductor industry. To date, most graphene nanodevices prepared in the laboratory continue to be fabricated on small manually exfoliated graphene sheets. This is because the crystal quality of these sheets is better than that of conventional CVD-grown graphene. Therefore, a breakthrough synthesis method for large-area ultra-high-quality CVD-grown graphene is crucial to translate the desirable properties of graphene into practical applications in the semiconductor industry.

To improve the quality of CVD-grown graphene, various strategies have been explored. These strategies include synthesizing (i) single-crystal graphene by single-nuclei preferential growth, (ii) adlayer-free graphene by Cu-substrate
carbon-removal pretreatment,\textsuperscript{197} and (iii) ultra-flat graphene by proton penetration.\textsuperscript{198} These techniques have resolved various problems in Cu-substrate CVD-grown graphene, leading to virtually perfect graphene. As a metallic 2D material, graphene must be transferred to an insulating substrate such that it can be applied to nanodevices;\textsuperscript{194} however, this unavoidably introduces contamination, cracks, folds, and unexpected doping.\textsuperscript{199} To resolve these problems, advanced graphene transfer methods have been proposed. These methods include replacing the commonly used PMMA with cellulose or paraffin,\textsuperscript{200,201} employing polymer-free transfer methods,\textsuperscript{202} and removing polymer residues by thermal treatment.\textsuperscript{203} Although these techniques improve the quality of transferred graphene, they remain difficult to implement for industrial applications because any transfer method inevitably degrades the graphene quality.\textsuperscript{204}

Hence, a straightforward strategy—the growth of graphene by direct synthesis on insulating substrates—was proposed. Some attempts have been made: (i) oxygen-assisted growth,\textsuperscript{205} (ii) molten-glass-substrate synthesis,\textsuperscript{206} and (iii) metal-substrate carbon dissolution.\textsuperscript{207} These methods enable the direct growth of polycrystalline nanographene on insulating substrates. However, compared with conventional Cu-substrate growth, they lack metal catalysts, epitaxial conditions, and layer-controlled mechanisms.\textsuperscript{208} Thus, graphene with extremely small domain sizes (~10–500 nm), uncontrolled layers, and inadequate crystal quality was obtained in practical nanodevices. Consequently, the foregoing has limited the application of graphene in practical nanodevices. Accordingly, the direct synthesis of wafer-scale high-quality single-crystal monolayer graphene on insulating
substrates is the most challenging yet critical task for enabling the use of graphene in high-performance nanodevices.

In this study, wafer-scale single-crystal Cu (111) on Al₂O₃ (0001) from commercial polycrystalline Cu foils was first synthesized by a long-term annealing phase conversion method using the strategy described in the previous section. This creates an ideal growth surface at the top Cu (111) foil and bottom Al₂O₃ (0001) substrate interface. At this interface, ultrahigh-quality single-crystal graphene films were synthesized by the MPE-CVD method. After the growth process, the Cu (111) foil was facilely exfoliated by liquid nitrogen-assisted extreme temperature difference separation method. Ultimately, the direct growth of adlayer-free wafer-level single-crystal monolayer graphene on insulating substrates using the MPE-CVD method was achieved.

5.2 Experimental Section

5.2.1 Graphene Growth via MPE-CVD

A schematic of the MPE-CVD system is shown in Figure 5.1. The growth process is described as follows. First, the long-term-annealed Cu (111)/Al₂O₃ (0001) is loaded into the MPE-CVD system. Next, the system in which pressure was controlled at 3 Torr was heated to 1075 °C; the H₂ and Ar flow rates were 50 and 350 sccm, respectively. Then, CH₄ flowing at 10 sccm was introduced into the tube during the carbon diffusion process. After 60 min, the system was cooled to 1050
°C for 30 min to reach the optimal growth temperature for high-quality graphene under the same gas mixture conditions.

Next, 10-sccm CH₄ gas (0.1 % diluted in Ar) was introduced into the system with flow rates of 10-sccm H₂ and 50-sccm Ar at 0.5-Torr pressure for 30 min. The purpose of introducing diluted CH₄ instead of pure CH₄ at this point was to maintain a high H₂–CH₄ gas flow ratio that reduced the net growth rate of graphene islands on the Cu (111) film surface. This ensured that the graphene film did not cover most of the Cu (111) film surface or its entirety. Thus, the decomposition of methane and dissolution of carbon atoms into the Cu (111) film were not hindered. The continuous flow of diluted CH₄ was found to provide the required carbon for graphene growth on Cu (111)/Al₂O₃ (0001). After the graphene growth, the system was gradually cooled to 300 °C for 20 min to prevent the Cu film from rapidly shrinking. Subsequently, the flow of CH₄ gas was stopped, and that of H₂ was increased to 30 sccm. The 200-W plasma unit was moved to the sample position and switched on for 3 min to clean graphene on the Cu upper surface. Meanwhile, the tube furnace was moved to the left side of the sample position and reheated to 1075 °C.

After the plasma etching process, the flows of H₂ and CH₄ gases were turned off, and the furnace was quickly moved back to the sample position. The sample was bound to be reheated to 1075 °C within 5 s. This rapid heating is presumed to prevent the possible etching of graphene islands at the Cu (111)/Al₂O₃ (0001) interface. Such etching may have occurred if the diffusion of H atoms through the
Cu (111) film continued over a longer period of heating. The growth cycle repeatedly occurred until the entire growth process was completed.
Figure 5.1 Schematic of MPE-CVD system consisting of conventional CVD system, plasma unit, precise pressure control system, and computerized intelligent automatic control system.

5.2.2 Liquid Nitrogen-Assisted Separation

After the MPE-CVD-synthesized growth, the liquid nitrogen-assisted separation method was applied to separate Cu (111) and graphene/Al₂O₃. After completing the entire growth process, the Cu (111)/graphene/Al₂O₃ (0001) samples were loaded into a liquid nitrogen separation system using a computer-controlled electromagnetically driven quartz rod connected to a quartz boat as carrier. A quartz tube with a cooling coil and small hole for liquid nitrogen injection was also designed, fabricated, and installed. Further, by moving the sample to the liquid nitrogen cooling area inside the quartz tube, the injected liquid nitrogen filled the coil surrounding the quartz tube and quartz boat at the end of the coil. Cooling was controlled using a liquid nitrogen pump and temperature control system. The quartz boat remained in this cooling zone for 30 min to stabilize the sample by complete immersion in liquid nitrogen at 77 K. Detailed measurements and analyses indicate that a certain amount of N₂ penetrated the interstitial region between the Cu (111) foil and sapphire during the immersion in liquid nitrogen. The tube furnace located on the right side of the cooling zone was heated to 500 °C within 30 min. After immersing the sample in liquid nitrogen for approximately 30 min, the cryogenic sample was rapidly moved to the 500 °C zone within 3 s and rapidly heated up to 500 °C; 1000-sccm Ar was allowed to flow into the quartz tube
as “protective” gas. The sample was maintained at 500 °C for 10 min; then, the oven was cooled to room temperature, and the sample was removed. The raised Cu (111) foil was easily peeled off by hand with tweezers, and graphene films were observed on the surface of the Al₂O₃ (0001) substrate.

### 5.2.3 Characterizations of As-Grown Graphene

In this study, the Raman spectra and mapping of graphene and hBN were obtained by confocal Raman spectroscopy (Alpha 300R, WITec) with laser wavelengths of 488 and 532 nm, irradiating metallic substrates and non-metallic substrates, respectively. For Raman spectroscopy, 600 and 1800 g/mm system gratings were used. Raman tests were performed using a lens with 100× magnification. All graphene morphologies in this study were observed using SEM (Merlin, Zeiss). Visible-light tests of graphene on Al₂O₃ were performed using a UV−visible (UV−Vis) spectrophotometer (Lambda 950, PerkinElmer) to measure the transmission spectra. The surface morphology and roughness of graphene were characterized by AFM (Dimension Icon, Bruker).

### 5.2.4 Dynamic Secondary Ion Mass Spectrometry

Depth profiling experiments were performed on a dynamic secondary ion mass spectrometry (SIMS) instrument (Hiden Analytical Company, Warrington, UK) operated under ultrahigh vacuum conditions (typically at 10⁻⁹ Torr). A continuous
Ar+ beam with 4-keV energy was used to sputter the surface. The selected ions were sequentially collected using a spectrometer (MAXIM) equipped with a quadrupole analyzer. The estimated raster of the sputtered area was $750 \times 750 \mu m^2$. To avoid the edge effect during the depth profiling experiments, ions were collected from a small area located in the middle of the sputtered area. With the use of adequate electronic gating, the acquisition area from which the depth profiling data were obtained was found to be approximately $75 \times 75 \mu m^2$. A constant sputtering rate was assumed. The sputtering time was converted to the corresponding sputtering depth by measuring the depth of the crater generated at the end of the depth profiling experiment using a stylus profiler (Veeco).

5.2.5 STM and LEED Characterization

Graphene on the sapphire samples was placed into an evacuated scanning tunneling microscopy (STM) vacuum chamber for more than 24 h. Ultrahigh vacuum STM measurements were performed in a cryogenic STM (SPECS Surface Nano Analysis GmbH) operating at 4.5 K and base pressure of $1.0 \times 10^{-10}$ Torr using a tungsten tip. Low-energy electron diffraction (LEED) with a beam diameter of approximately 1 mm was performed in an ultrahigh vacuum chamber base pressure: $1.0 \times 10^{-10}$ Torr). To prevent the insulating substrate from charging, a dual multi-channel plate LEED (OCI Vacuum Microengineering) was used. A molybdenum mask was employed to be in contact with the graphene layer at the top, thus preserving the circular measurement area. In addition, a distortion
correction of LEED images was performed using the LEED Lab and LEED Cal software.

5.3 Multi-Cycle Plasma Etching-Assisted CVD Growth Process

As mentioned in Chapter 4, during the long-term near-melting temperature annealing process, polycrystalline Cu transformed to Cu (111). Moreover, the Cu foil gradually tightly adhered to the upper surface of Al₂O₃ (0001), resulting in a slight gap between Cu (111) and Al₂O₃ (0001). This extremely small gap prevents the entry of methane molecules from the edges of the Cu (111) foil, thus avoiding the formation of inferior fractal graphene. To confirm this, a comparative experiment on the rapid graphene growth is performed, as shown in Figure 5.2. Copper that was not subjected to long-term annealing was placed on sapphire, and other substrates were set on Cu (111)/Al₂O₃ (0001) that underwent long-term annealing. After the conduct of fast CVD-synthesized graphene growth experiments, graphene was observed on both the upper and lower surfaces of the unannealed polycrystalline Cu. However, no graphene was observed at the long-term-annealed Cu (111)/Al₂O₃ (0001) interface. This illustrates that in this substrate structure, carbon atoms can only diffuse through the Cu (111) film surface to the interface between Cu (111) and Al₂O₃ (0001). Hence, they are the source of graphene growth, nucleation, and epitaxial growth of monolayer graphene.
Figure 5.2 Comparison of fast CVD-synthesized growth using unannealed Cu/Al₂O₃ and annealed Cu (111)/Al₂O₃. (a) Schematic of graphene formation by edge-diffusion growth mode in CVD when Cu/Al₂O₃ gap is large. (b) Photograph of unannealed Cu/Al₂O₃ before growth. (c) Graphene formation on gap side of Cu/Al₂O₃. (d) Raman signal of graphene detected from position in (c). (e) Schematic of forbidden entry of methane due to extremely thin gas. (f) Annealed Cu (111)/Al₂O₃ before growth. (g) No graphene formed on gap side of Cu foil. (h) No detected graphene signal in (g).

As previously reported, the bottom surface of the long-term annealed Cu (111) was smooth. This reduced the graphene nucleation density and increased the single-domain size of graphene, thus preventing the formation of nanographene and amorphous graphene. In addition to surface smoothing, the strong van der Waals interactions between Cu (111) and Al₂O₃ (0001) were considered. Moreover, Cu (111) and Al₂O₃ (0001) had similar hexagonal lattice symmetries and small lattice mismatches, leading to the uniform superlattice potential at the interface. Under
this superlattice potential, carbon atoms nucleate under and form graphene with the same crystalline phase. Subsequently, they further grow and merge to form monolayer single-crystal graphene films. Accordingly, the interface between Cu (111) and Al₂O₃ (0001) is considered as an ideal platform for the synthesis of single-crystal graphene.

Herein, the MPE-CVD growth process is discussed in detail. The annealed Cu (111)/Al₂O₃ (0001) heterostructure was used as a substrate to initiate graphene synthesis in the MPE-CVD system. As shown in Figure 5.3, the synthesis proceeds in four stages: (i) carbon diffusion, (ii) graphene growth, (iii) plasma cleaning, and (iv) Cu removal.

In the first stage, active carbon atoms were formed by Cu (111)-catalyzed methane decomposition. Some of these carbon atoms moved freely on the Cu surface and condensed into graphene islands. In addition, some of them dissolved in the Cu (111) foil, forming a Cu–C alloy. The difference in carbon concentration between the upper and lower surfaces of the Cu film is significant. In view of this, based on
the osmotic theory, carbon atoms can diffuse through the Cu (111) foil to the interface between Cu (111) and Al₂O₃ (0001), acting as a carbon source for graphene growth at the interface.

In the second stage, the diffused carbon atoms gradually nucleate, grow epitaxially at the interface, and subsequently form graphene. Graphene nuclei with the same crystal orientation are formed under the action of uniform superlattice potential generated by the lower surface of Cu (111) and the upper surface of Al₂O₃ (0001). This leads to the final formation of aligned graphene domains. In addition, the long-term hydrogen annealing pretreatment in the single-crystal Cu conversion stage virtually completely eliminated the carbon species from the Cu (111) foil, leading to the formation of adlayer-free graphene at the interface. However, as mentioned, graphene also forms on the top surface of the Cu (111) foil, preventing carbon diffusion and reducing the catalytic efficiency of the growth process.

Accordingly, in the third stage, a hydrogen–argon plasma is employed to etch and remove graphene that forms on the top surface of the Cu (111) foil, as shown in Figure 5.4. During the cleaning process using plasma, hydrogen plasma could not enter the interface owing to the plasma shielding effect of the metallic material. This prevented the hydrogen plasma from damaging graphene at the interface. However, because hydrogen molecules can diffuse into the interface and etch the interfacial graphene at high temperatures, the CVD system was rapidly cooled to 300 °C during the plasma cleaning process. In the typical CVD-synthesized growth of Cu substrates, significant Cu shrinkage causes graphene wrinkling during
cooling. However, because of the support provided by Al$_2$O$_3$ (0001), graphene shrinkage was not substantial during the cooling process, thus preventing wrinkle formation.

By repeating the three stages (multiple cycles), wrinkle-free monolayer single-crystal graphene was synthesized at the interface. In the fourth stage, after the completion of graphene growth at the interface, the upper Cu foil was separated using the extreme temperature difference separation method assisted by liquid nitrogen (described in the next section). This yielded a high-quality single-crystal monolayer graphene grown on an Al$_2$O$_3$ (0001) substrate.

Single-crystal graphene islands at the Cu (111) and Al$_2$O$_3$ (0001) interfaces were prepared for the clearer observation and characterization of graphene. As shown in Figure 5.5, after 10 growth cycles under specific conditions, single-crystal graphene islands have been directly synthesized in Al$_2$O$_3$ (0001) by the MPE-CVD method.
Figure 5.4 Plasma etching experiments considering various times and distances. (a)–(d) Optical micrograph of graphene (white) distribution during plasma treatment time; Cu foil was oxidized for better contrast. (e)–(f) Comparison of sample before and after 3-min plasma treatment; graphene is totally removed in (f). (g) Optical micrograph of graphene (white) distribution with distance to center of plasma unit; inserts show corresponding Raman spectra.
Figure 5.5 Parameters of Cu annealing and graphene MPE-CVD-synthesized growth. (a) Time evolution diagram of gas flow and temperature of MPE-CVD process for one growth cycle. Inset shows computer record of gas flow and temperature for 15 growth cycles of MPE-CVD process. (b) Growth parameters of temperature, pressure, time, and gas flow in MPE-CVD system. 1st period: 1075 °C, 3 Torr, 60 min (50-sccm H2, 10-sccm CH4, and 350-sccm Ar); 1st to 2nd period: temperature from 1075 to 1050 °C (linear with time) and total time = 30 min; 2nd period: 1050 °C, 0.5 Torr, 30 min (10-sccm H2, 10-sccm diluted CH4, and 50-sccm Ar); 2nd to 3rd period: temperature from 1050 to 300 °C for 20 min; 3rd period: 300 °C, 1 Torr, plasma = 200 W for 3 min (30-sccm H2 and 50-sccm Ar); 3rd to 1st (next cycle) period: temperature from 300 to 1075 °C in 5 s.
The figure also shows that the graphene islands have the aligned orientation. Each graphene island exhibits a standard hexagonal shape and sharp edges, indicating the high lattice quality of the grown graphene, as shown in Figure 5.6(a).

Raman characterization of the prepared samples was performed to further investigate the quality of the grown graphene. Uniform Raman mappings of the $I_D$--$I_G$ ratios were obtained. This indicates that graphene grown at the interface is considerably homogeneous and virtually defect-free, as shown in Figure 5.6(b). Furthermore, the full width at half maximum (FWHM) of the 2D peak in the Raman map is approximately 28 cm$^{-1}$, which is typical for monolayer graphene. This confirms that the formed graphene has no adlayers and is monolayer graphene, as shown in Figure 5.6(c). The foregoing Raman spectroscopy results indicate that the directly grown graphene has excellent crystal structure and quality. Raman single spectra were also collected based on typical Raman spectra. Compared with the peak of transferred graphene, a significant blue shift in the 2D peak of graphene grown directly on Al$_2$O$_3$(0001) is observed, as shown in Figure 5.6(d). This reveals a strong van der Waals interaction between graphene and the Al$_2$O$_3$(0001) substrate.

The 2D peaks of graphene grown on Cu (111) are also observed to be more blue-shifted than those of graphene grown directly on Al$_2$O$_3$(0001), as shown in Figure 5.6(e). This indicates a strong interaction between graphene grown on the upper surface and Cu (111). Furthermore, as shown in Figure 5.6(f), the statistical distributions of 2D FWHM and $I_{2D}$--$I_G$ ratios of Raman signals are also calculated.
The results indicate that graphene grown on Al$_2$O$_3$(0001) has high crystal quality and no adlayers.

Figure 5.6 (a) Optical micrograph of graphene islands on Al$_2$O$_3$(0001); orientation of aligned hexagonal islands indicated by dashed lines. (b) Raman map of $I_D$–$I_G$ ratios of graphene island shown in (a). (c) 2D FWHM Raman map of graphene island in region shown in (a). (d) Representative Raman spectra of graphene on Al$_2$O$_3$ (red); graphene grown on upper surface of Cu film without transfer after removing Cu fluorescence (black); graphene grown on upper surface of Cu(111) film and then transferred to Al$_2$O$_3$(0001) (blue) and 300-nm SiO$_2$/Si wafer (green). (e) 2D peak blueshift of four types of graphene mentioned in (d). 2D peak position of graphene transferred onto SiO$_2$/Si base is considered as reference. (f) 2D peak FWHM and $I_{2D}$–$I_G$ ratio of 20 samples of each type of graphene mentioned in (d).
5.4 Cu Film Deformation Using Liquid Nitrogen

After the MPE-CVD-synthesized growth, the Cu/graphene/sapphire sample was completely immersed in liquid nitrogen for 30 min. Then, within 3 s, the sample (with liquid nitrogen “attached”) was moved to a high-temperature zone (i.e., 500 °C). The sample was transferred under atmospheric pressure and with “protective” argon gas flow in the quartz tube heated to 500 °C. It was left in the 500 °C zone for 10 min and then cooled to room temperature. The Cu foil is found to be significantly deformed (i.e., with “bulges”) and can be easily peeled off with tweezers. To verify the foregoing, the liquid nitrogen separation and reheating experiments were repeated; fundamentally the same results were obtained.

An investigation of the underlying mechanism led to the following explanation. During the long-term annealing process at 1075 °C, the Cu foil becomes extremely thin (i.e., micrometer-scale thickness). As discussed in the previous section, the polycrystalline Cu foil can transform into a single-crystal Cu (111) foil on an Al₂O₃(0001) substrate. At 1075 °C, the Cu (111) layer is presumed to “conform” with the perfect epitaxy on the Al₂O₃(0001). However, when the sample is finally cooled to room temperature (25 °C), the extremely large temperature change causes the Cu foil to shrink substantially (assuming that the foil does not "adhere" well to the sapphire) by approximately 2.0 %. Meanwhile, the “freely floating” sapphire substrate undergoes biaxial contraction of approximately 0.73 %. Consequently, if de-adhesion does not occur at certain locations, interfacial stress (approximately 1.5 GPa) builds up at the interface.
In a highly improbable situation in which perfect adhesion remains during cooling, tremendous tensile stress on the Cu (111) foil and compressive stress on sapphire at the interface occur. Because the sapphire substrate is 1-mm thick and rigid, it does not deform. In contrast, because the Cu foil is thin, the “buildup” in interfacial stress leads to de-adhesion. The tensile stress acting on the 1–2-µm-thick Cu(111) is considerably higher than the stress required for a free Cu (111) foil to plastically deform, particularly at elevated temperatures. In measuring the tensile loading of the Cu (111) foil at room temperature, the onset of plastic deformation was found to occur at approximately 30 MPa. This deformation (which leads to de-adhesion) seems possible to occur at 900 °C or higher as the sample cools from 1075 °C. Although the details on how the de-adhesion of the Cu (111) layer occurs, the observation of the interlayer spacing provides strong evidence that it does not occur in many locations between the Cu (111) layer and Al₂O₃(0001) substrate.

Thus, during the immersion of sample in liquid nitrogen, the N₂ molecules penetrate the gaps (which are present because of the de-adhesion described above) between the Cu (111) foil and sapphire wafer possibly as a thin liquid layer. After approximately 30 min, the sample with a temperature value of 77 K was transferred to the 500-°C zone within 3 s; it rapidly heated to 500 °C. The 11-fold change in absolute temperature (from 77 to 773 K) caused volume expansion, thus forming bulges “in” the Cu foil (“on” the upper surface) due to the pressure exerted by the expanding N₂ gas.
To explore the role of “trapped” \( \text{N}_2 \) molecules in deforming the Cu foil, several experiments were conducted, and measurements were performed to determine whether \( \text{N}_2 \) is “in the gap” between the Cu (111) foil and sapphire surfaces. If \( \text{N}_2 \) molecules enter the Cu foil and sapphire during the sample immersion in liquid nitrogen, then the rapid heating to 500 °C causes \( \text{N}_2 \) to exert sufficient pressure, forming bulges in the Cu foil at various locations, as illustrated in Figure 5.7.

**Figure 5.7** Schematic of Cu foil deformation during “liquid nitrogen separation process.” \( \text{N}_2 \) molecules trapped in the “gap” are possibly liquid at 77 K; however, experimental proof is not available. Hence, the trapped molecules may also be in gas-like state.

To test whether \( \text{N}_2 \) molecules are present in the gap between the Cu (111) foil and sapphire after removing the sample from liquid nitrogen, the sample was “moved”
as swiftly as possible from the liquid nitrogen bath to a Raman spectrometer. Then, the Raman spectra at the interface between Cu and sapphire were obtained.

The experimental details are described below. We choose a “good sample” of Cu/graphene/sapphire in which Cu (111) closely adheres to the sapphire (the sample appears similar to a mirror viewed from the backside, i.e., viewing through from the sapphire side). A Raman microscope with a 532-nm laser and 50× lens was used. Before dipping the sample into liquid nitrogen, the Raman laser was focused on the interface between the Cu(111) foil and sapphire of this sample, and a Raman spectrum was obtained at the interface (again, sapphire was facing up). The sample was then entirely immersed in liquid nitrogen for 30 min. Subsequently, we pulled out the sample and quickly placed it on the Raman stage. Then, the Raman spectrum of the sample with the same configuration used in the control measurement prior to sample immersion in liquid nitrogen was obtained.

Before immersion in liquid nitrogen, no Raman signal was observed for the N\textsubscript{2} molecules at the interface. Several positions with a focal plane at the interface were randomly chosen; none had any intensity at the peak position for N\textsubscript{2}. After the immersed sample was swiftly moved to the Raman spectrometer, a Raman peak at 2330 cm\textsuperscript{−}1 (peak position of N\textsubscript{2}) was detected at the interface between Cu (111) and sapphire (Figure 5.8). The intensity of this peak diminishes with time; this is inferred due to the diffusion of N\textsubscript{2} molecules out of the small gap between the foil and sapphire.
Figure 5.8 Raman peaks indicating possible presence of N$_2$ at interface between Cu foil and sapphire substrate.

Figure 5.9 shows the control experiments involving “surface-sealed” and “edge-sealed” samples in which PMMA is used to seal (i) the four edges of the Cu foil on sapphire or (ii) the surface of the Cu foil but not the edges. After sealing, the Raman experiments above were repeated for each configuration. The two samples used in the experiments were prepared as follows. Tape was utilized as a mask to cover (i) the surface or (ii) edges of samples; then, PMMA was spin-coated on the two samples. After removing the mask, each sample (in separate experiments) was immersed in liquid nitrogen for 4 min and then the sample was swiftly removed. The following were observed: (i) the edge-sealed sample did not exhibit N$_2$ Raman signals; however, (ii) the surface-sealed sample exhibited N$_2$ Raman signals. This suggests that the N$_2$ molecules entered the gap through the edges when the sample was immersed in liquid N$_2$. 
5.5 DFT Calculation of Graphene Binding Energy

To gain insight on the growth mechanism of graphene on the interface between Cu (111) and Al₂O₃ and thus obtain theoretical support, DFT calculations were performed. A theoretical model for Cu (111)/graphene/Al₂O₃ (0001) was designed, and the energy of graphene after the relaxation state was calculated. The calculation results show that the carbon-binding energies of graphene at the Cu (111), Al₂O₃ (0001), and Cu (111)/Al₂O₃ (0001) interfaces are 0.204, 0.200, and 0.304 eV, respectively. This indicates the possibility of graphene growth at the interface, as shown in Figure 5.10.
Two models were further constructed using Cu (111), graphene, O-terminated Al₂O₃ (0001), and Al-terminated Al₂O₃ (0001) as model surfaces (i.e., Cu (111)/graphene/O-terminated Al₂O₃ (0001) and Cu (111)/graphene/Al-terminated Al₂O₃ (0001). Calculations showed that the binding energies of graphene on O-terminated and Al-terminated Al₂O₃ (0001) were 0.304 and 0.081 eV per carbon atom, respectively. An interesting phenomenon was also observed when the Cu atoms in this system were examined: the Cu stacking energy decreased significantly with the formation of graphene. As shown in Figure 5.11, this phenomenon further enhances the Cu (111)/graphene/Al₂O₃(0001) structure.
Figure 5.11 Atomic structures and DFT simulations of Cu (111) and graphene on Al-terminated and O-terminated Al₂O₃ (0001). (a) Comparison of atomic structures of graphene between Cu (111) and O-terminated Al₂O₃ and between Cu (111) and Al-terminated Al₂O₃ after relaxation; Cu, Al, O, and carbon atoms are shown in gold, blue, red, and black colors, respectively. (b) Binding energies per carbon atom in abovementioned models. (c) Stacking energies per Cu atom in abovementioned models.

In addition to the foregoing DFT simulations, the mechanisms of carbon atom distortion during graphene growth are analyzed, as shown in Figure 5.12. During the MPE-CVD-synthesized growth process, a small quantity of active carbon atoms catalyzed by methane decomposition is dissolved into the Cu foil at high temperatures and gradually diffuses through the foil to the Cu (111)/Al₂O₃ (0001) interface.²¹²
This dissolution and diffusion processes were studied based on Fick’s law and finite element simulations of the convective diffusion equation. The diffusion of carbon in Cu over time was simulated. The simulation results show that the carbon diffusion process is extremely sensitive to the annealing temperature, implying that graphene synthesis requires a precise control of each CVD parameter. Based on this, the MPE-CVD method was tuned using a specially designed temperature-varying carbon dissolution strategy to ensure continuous carbon atom diffusion. Furthermore, considering the similar crystal symmetries of Cu (111), graphene, and Al$_2$O$_3$ (0001), as well as the crystal symmetry and small lattice mismatch between Cu (111) and Al$_2$O$_3$ (0001), the formation of a moiré superlattice structure was observed when the two materials were stacked at torsion angles of 0° and 60°, respectively. Under these conditions, graphene
domains were grown in the same crystal orientation and subsequently merged to form single-crystal graphene films between Cu (111) and Al₂O₃ (0001). When a graphene layer was inserted into Cu (111) and Al₂O₃ (0001), a new moiré pattern was formed (Figure 5.13). This observation is significant for our subsequent study of the physical properties using different stacking methods.

Figure 5.13 Schematic of sandwich structure formed by Cu (111), graphene, and Al₂O₃ (0001), showing moiré superlattice pattern with 60° twist angle among layers.

### 5.6 Inch-Size Single-Crystal Graphene Grown on Sapphire

As presented in the previous chapter, the graphene islands grown at the interface of Cu (111) and Al₂O₃ (0001) have the same orientation. This means that if the experimental parameters are tuned and graphene at the interface is allowed to grow continuously, graphene islands with the same orientation can merge to form
a large-area single-crystal monolayer graphene. Accordingly, the wafer-scale single-crystal monolayer graphene on an Al₂O₃ (0001) substrate were successfully synthesized by optimizing the growth parameters involved in MPE-CVD. The graphene/sapphire sample is compared with the pristine sapphire sample, as shown in Figure 5.14(a). The figure indicates that the light absorption of Al₂O₃ with graphene coverage is higher than that of the pristine Al₂O₃ (0001) wafer. To further quantify its light transmission, UV–Vis light absorption tests were performed on Al₂O₃ with graphene and pristine Al₂O₃; graphene/Al₂O₃ exhibited greater visible light absorption in the UV–Vis transmission spectrum.

Furthermore, as determined by the Raman spectral analysis, the I₂D–I_G ratio and 2D peak FWHM indicate that the as-grown wafer-scale graphene film is an adlayer-free high-quality monolayer. The surface roughness measured from the entire wafer area represents the flat characteristic of the as-grown graphene on this sapphire wafer, as shown in Figure 5.14(b). The optical micrographs and Raman maps of the 2D peak FWHM revealed the wrinkle-free surface of graphene grown on Al₂O₃. In contrast, graphene grown on the upper surface of Cu (111) and transferred to SiO₂/Si exhibits visible wrinkles, as shown in Figure 5.14, (c) and (d). Based on the SEM images, graphene grown on Al₂O₃ (0001) has a uniform surface without any adlayer or noticeable wrinkles, whereas the SiO₂/Si-based transferred graphene exhibits a distinct wrinkle network, as shown in Figure 5.14, (e) and (f). Graphene surfaces were analyzed by AFM; a smooth surface for graphene grown on Al₂O₃ and a rough surface with distinct wrinkles for the transferred graphene are observed, as shown in Figure 5.14.
5.14(h), HR-TEM images show the clean surface of graphene grown on Al$_2$O$_3$. Moreover, the crystal lattice orientations determined from the SAED patterns obtained from various locations indicate a highly consistent single-crystalline structure of the as-grown graphene.

![Figure 5.14](image)

**Figure 5.14** (a) Photograph and UV–Vis transmittance spectra in 350–800-nm wavelength range of Al$_2$O$_3$ (0001) wafer without graphene (left) and with as-grown graphene (right). (b) Raman signals of I$_{2D}$–I$_G$ intensity ratio (cyan) and 2D peak FWHM (magenta) (left); surface roughness of graphene grown directly on Al$_2$O$_3$
and upper surface of Cu (111) film and transferred to Al₂O₃ measured by AFM (right). (c) Optical image (left) and Raman map of 2D peak FWHM (right) of graphene grown directly on Al₂O₃ (0001). (d) Optical image (left) and Raman map of 2D peak FWHM (right) of graphene on Cu (111) and then transferred onto SiO₂/Si substrate. Wrinkles are indicated by arrows. (e) SEM image of graphene grown on Al₂O₃ (0001). (f) SEM image of graphene grown on upper surface of Cu (111) and transferred to SiO₂/Si. (g) AFM image of graphene grown directly on Al₂O₃ (0001) (left) and transferred SiO₂/Si-based graphene (right). Height profiles along marked line are plotted in bottom inset. (h) HR-TEM image of directly grown graphene.

To experimentally confirm that the grown graphene is a single crystal over a large area, controlled experiments are designed and performed, as shown in Figure 5.15. Through oxygen plasma etching and grain boundary oxidation experiments, the defects were found to be uniformly random on the graphene surface rather than clustered in certain boundary regions. This verifies the single-crystal nature of the grown graphene films.
Figure 5.15 Oxygen plasma etching and chemical-assisted grain boundary oxidization experiments. (a) Schematic of oxygen plasma etching experiment. (b) Monochrome micrograph of graphene on Al2O3 surface. Graphene uniformly damaged by weak oxygen plasma. (c) Monochrome micrograph of transferred polycrystalline graphene on Al2O3 surface. (d) Raman spectra of graphene (red cross in (c)) and damaged areas (blue cross in (b)). (e) Schematic of chemical-assisted grain boundary oxidization. Directly grown single-crystalline graphene and Cu-substrate grown polycrystal graphene transferred to polished Cu foil. Oxidization treatment was conducted in salt humid environment. (f) Monochrome micrograph of graphene grown on Cu (111)/Al2O3 (0001) interface and transferred from sapphire to polished Cu foil. Virtually no grain boundaries were observed; thus, single-crystalline graphene was grown. (g) Micrograph of Cu substrate-grown polycrystalline graphene. Many grain boundaries are etched, and CuOx formed in those regions in polycrystalline graphene. (h) Raman spectra from no-CuOx area (blue cross in (f)) and CuOx area (red cross in (g)).

To directly observe the single crystallinity of as-grown graphene on Al2O3, LEED was applied.215-217 The LEED patterns obtained are uniform over the entire measured sample area, as shown in Figure 5.16. The figure shows a single hexagonal structure, thereby supporting the single crystalline growth of graphene. Graphene adopts a higher-order commensurate registry in which the relationship with the substrate can be described as a 2 × 2 supercell of the graphene lattice directly matching the sapphire lattice. In addition, the presence of a graphene layer on the sapphire substrate was confirmed using low-temperature STM; atomically resolved images of the graphene lattice from different sample regions were obtained. The fast Fourier transform (FFT) of scans reveal a uniform lattice
orientation. Moreover, the several low-intensity frequencies that do not correspond to graphene (Figure 5.17) are attributed to moiré contrast.

By combining the Raman, SEM, TEM, STM, and LEED characterization techniques, the grown graphene is verified to be a single-layer single-crystalline high-quality graphene.

**Figure 5.16** LEED characterization of graphene film (grown at Cu (111)/Al$_2$O$_3$ (0001) interface) on Al$_2$O$_3$ (0001). (a)–(b) LEED patterns were obtained from two regions (4 mm apart) of graphene film on Al$_2$O$_3$ (0001) surface. Both images show identical hexagonal pattern with the same orientation, indicating that as-grown graphene is single crystal and corresponds with Al$_2$O$_3$ (0001) surface. (c) Tilted LEED measurement with overlaid simulations (applying geometric scattering theory) featuring lattice vectors of Al$_2$O$_3$ (0001), its expected spot position is color red and that for epitaxial graphene is color purple). All depicted images are contrast-inverted.
Figure 5.17 STM characterization of graphene film on Al₂O₃ (0001). (a)–(b) Atomic-resolution STM images. (c)–(d) FFTs of STM images overlaid with reciprocal graphene lattice vectors and some corresponding spot positions (purple) with several moiré spots highlighted (magenta).

5.7 Conclusion

Currently, the synthesis of high-quality graphene on insulators is one of the most interesting topics for many scientists. In this study, a unique interface between sapphire and Cu (111) for graphene growth is designed based on the single-crystal Cu (111) fabrication. Multiple physical mechanisms (such as carbon diffusion, superlattice potential confinement, graphene adlayer suppression, and different thermal expansion coefficients) were utilized. Consequently, the direct growth of adlayer-free wafer-scale single-crystal monolayer graphene on insulating substrates by the MPE-CVD method was achieved. A sufficient number of characterization methods, such as optical characterization, Raman spectroscopy,
SEM, TEM, STEM, EDS, AFM, XRD, LEED, STM, and SIMS, were employed to observe and confirm the direct growth of wafer-scale single-crystal graphene on insulating substrates. Additional essential experiments were performed to support the experimental results. These include Cu-substrate oxidization treatment, fast growth by CVD, oxygen plasma etching, and chemical-assisted grain boundary oxidization experiments. Finite element simulations and DFT calculations were performed to explore the underlying physical mechanisms and provide theoretical support for the experimental results.

This work provides an approach for directly synthesizing high-quality graphene on insulating substrates. This direct growth method compared with the conventional technique of growing graphene on a Cu-substrate avoids secondary contamination and damage during the transfer process. As-grown graphene can be used in high-performance nanodevices. Moreover, the realization of large-area single-crystalline graphene films provides an ideal 2D substrate for the epitaxial growth of other wafer-scale 2D materials and formation of van der Waals heterostructures. Consequently, the development of CVD synthesis of wafer-scale single-crystalline 2D materials is accelerated. This study overcomes the hindrance in the industrial production and use of graphene in insulators, opening the opportunity for the emergence of graphene-based electronics and semiconductor nanodevices. As a breakthrough in graphene synthesis, this direct growth technique enables the wafer-scale production of next-generation high-performance graphene-based integrated electronics and promotes the potential of graphene in various fields.
Chapter 6 Conclusion and Future Work

6.1 Conclusion

This study achieved the controlled CVD-synthesized growth of graphene, hBN, and MoS$_2$ with tunable domain shapes and crystal qualities. An in-depth study of the underlying physical mechanism of the CVD-synthesized growth of these 2D materials was performed. Based on the traditional fractal theory, 2D DLA growth models were constructed for the CVD-synthesized growth mechanism of graphene and other 2D materials considering all influencing factors. By comparing the simulation and experimental results, perfect consistency between simulations and experiments on the CVD synthesis of graphene, hBN, and TMDs was observed.

Through further exploration, the SD-NGR was found to play a crucial role in controlling the crystal shape and quality of 2D materials. Accordingly, guided by this model and related theory, the influencing parameters of CVD-synthesized growth were precisely and directionally manipulated. This manipulation adjusted the SD-NGR to finally achieve the controllable synthesis of as-grown 2D materials with single-crystal morphology and lattice quality. Molecular dynamic simulations were employed to predict the CVD-synthesized growth of 2D materials, such as graphene and hBN. Raman spectroscopy and SEM were applied to systematically characterize the as-grown graphene, hBN, and MoS$_2$ by examining their crystal shapes and qualities. This work established the foundation for the subsequent precise tuning of morphologies, crystal qualities, and physical properties of CVD-grown 2D materials. Hence, it creates a basis for further research on the growth of
high-quality wafer-scale 2D materials for scientific research and industrial applications.

A large-area single-crystal Cu (111) foil was also successfully prepared. The stable energy state of single-crystal Cu (111) on the c-plane sapphire was also theoretically verified by DFT calculations. After stacking the cleaned or pretreated sapphire substrates and pre-polished commercial as-received polycrystalline Cu foils through a long-term high-temperature H₂ environment annealing process, polycrystalline Cu was gradually transformed into single-crystalline Cu films and adhered to the sapphire substrates. The resulting Cu foil and sapphire substrate formed an atomically smooth and tight contact surface.

The absence of distinct grain boundaries on the Cu surface was examined using optical microscopy and SEM. In addition, the crystallinity of polycrystalline and single-crystal Cu was tested using EBSD with IPF maps and XRD measurements. The surface roughness of Cu after annealing was measured using AFM. Finally, a cross-sectional sample was prepared using FIB, and the interface was observed at the atomic-level resolution using HR-TEM. The preparation of large-area single-crystal Cu foil is essential for the wafer-scale CVD synthesis of graphene and other 2D materials.

Based on the study of the preparation of single-crystal Cu (111), the wafer-scale high-quality single-crystal monolayer graphene growth on insulating sapphire substrates was achieved via the proposed MPE-CVD growth method. First, an ideal interface was created by fabricating a single-crystal Cu (111) foil on Al₂O₃
(0001) substrates. By relying on the superlattice potential confinement at the interface, pre-removal of carbon species, and metal–insulator interface growth, the adlayer-free ultra-flat single-crystal graphene with excellent electronic properties was directly synthesized at the interface. This single-crystal graphene remained on the insulating substrate after the upper layer of the Cu (111) film was detached.

Raman spectroscopy, SEM, and AFM were used to characterize the uniformity of the as-grown monolayer graphene. To determine the crystal quality and confirm the crystallinity, HR-TEM, SAED, STM, and LEED were used. As a breakthrough in the field of graphene synthesis by CVD, this graphene direct growth technology enables the industrial-level production of next-generation high-performance graphene-based integrated electronics. Moreover, it facilitates the attainment of the potential of graphene in various fields.

6.2 Future Work

6.2.1 Achieving Fast Graphene Growth on Insulators

Growing graphene on insulating substrates is currently one of the main directions of research because many opportunities and possible applications worthy of investigation remain unexplored. To date, with this study, the growth of graphene on sapphire substrates over a large area though CVD synthesis was achieved. However, the current growth strategy requires multiple growth cycles and involves complex physical mechanisms related to many fields. A considerable amount of
time is necessary to complete the entire growth process. Moreover, it is a highly demanding operation.

Hence, devising an efficient and simple method to grow graphene directly on insulator substrates is extremely beneficial. Because of the urgent demand for the industrial production of graphene, new techniques to obtain highly efficient wafer-scale graphene on insulators must be explored. Accordingly, work is ongoing to formulate new growth strategies that differ from those previously reported with the goal of achieving fast graphene growth on insulating substrates. Based on experience in previous studies, improving the efficiency of graphene growth by modifying the upper-layer metal film is under consideration. The presumption is that this adjustment will enable the rapid growth of graphene on insulating substrates. The direct fast growth of graphene on insulating substrates will certainly provide graphene with a vast application range and resolve many bottleneck problems confronting its use. Evidently, the further development of CVD-synthesized growth methods and strategies to grow graphene on insulating substrates is necessary.

6.2.2 Growth of Multilayer Graphene on Insulating Substrates

In addition to single-layer graphene, the growth of bilayer, trilayer, and multilayer graphene systems is of interest. Multilayer graphene systems can exhibit various new physical properties owing to the different twist angles among layers. These can be used to study new physical phenomena or applied to moiré nanodevices.
Currently, the direct growth of single-layer graphene on insulating substrates has been achieved.

Bilayer and multilayer graphene have been reported to have exceptional properties, many of which are not found in monolayer graphene; however, they are not easy to grow directly on insulator substrates. Therefore, the preparation of bilayer or multilayer graphene on different substrates is currently being attempted by many researchers. Because the growth mechanism of bilayer graphene is not similar to that of CVD-grown monolayer graphene, new growth methods are being explored to achieve the direct growth of bilayer or multilayer graphene on insulating substrates.

If bilayer or multilayer graphene can be grown directly on insulating substrates and the stacking modes among layers are investigated, then the study of the graphene bandgap for future graphene applications in the semiconductor nanodevice field can be initiated.
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APPENDICES B: Permission Letters

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