

Achieving Ultraclean Graphene: Characterization and Applications

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ABSTRACT

Maintaining the cleanliness of graphene remains one of the most critical challenges for realizing its full potential for advanced electronic and quantum applications.

Contaminants introduced during synthesis, transfer, and handling can obscure intrinsic properties and hinder atomic-scale characterization. We approach the goal of making graphene ultra-clean through the development of polymer-free transfer and in-situ radical-cleaning techniques. Two complementary transfer methods were established. A polymer-free exfoliation technique using Ni/In/Cu stacks was developed to transfer epitaxial graphene grown on SiC substrates without introducing organic residues. In contrast, a metal-assisted transfer approach employing a thin Pd interlayer was demonstrated for CVD-grown graphene, enabling polymer-free transfer onto SiO₂ and other robust substrates while preserving surface integrity. Both methods eliminated polymer contamination and, in the case of epitaxial graphene, simultaneously removed surface adlayers during transfer. To further enhance cleanliness, an in-situ electron-beam-induced radiolysis process was developed, in which water radicals generated within the transmission electron microscope react with hydrocarbon residues to form volatile products. This process effectively removed organic contaminants without damaging the graphene lattice, yielding atomically clean regions hundreds of nanometers wide. Characterization using scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) confirmed the exceptional cleanliness and structural integrity of the resulting graphene. Finally, ultra-clean graphene was explored as an interfacial layer for remote epitaxy on GaSb substrates, demonstrating the feasibility of transferring clean graphene to chemically sensitive materials. The combination of

polymer-free transfer, metal-assisted exfoliation, and in-situ radical cleaning provides a scalable, reproducible route to fabricate ultra-clean graphene suitable for next-generation electronic and quantum device applications.

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CHAPTER ONE

INTRODUCTION AND GENERAL INFORMATION

1.1 Introduction

Graphene, a two-dimensional allotrope of carbon, has attracted significant scientific and technological interest since its discovery in 2004 due to its exceptional electrical, mechanical, and thermal properties. Its unique band structure, in which charge carriers behave as massless Dirac fermions, enables extraordinary carrier mobility, optical transparency, and mechanical strength. These properties position graphene as a promising material for next-generation electronic, photonic, and metrological applications.

However, realizing its full potential remains hindered by the persistent issue of contamination and structural defects introduced during synthesis, transfer, and subsequent processing.

Organic residues originating from polymer-assisted transfer methods and environmental hydrocarbons are particularly problematic, as they degrade electronic performance and obstruct atomic-level characterization. Traditional cleaning strategies often damage the delicate monolayer structure, making it challenging to achieve large, defect-free, and contamination-free regions of graphene. Therefore, developing robust methods for producing and maintaining ultra-clean graphene is essential for advancing both fundamental research and practical applications.

This thesis addresses these challenges by introducing polymer-free transfer methods for chemical vapor deposition (CVD)-grown and epitaxial graphene, along with an in-situ cleaning approach based on electron-beam-induced water radiolysis. Together, these techniques enable the preparation of large, suspended, ultra-clean graphene regions

suitable for advanced characterization and device applications. Beyond fabrication, this work also explores the role of ultra-clean graphene in remote epitaxy and its potential for quantum Hall devices, highlighting its significance for flexible electronics and quantum metrology.

1.2 Thesis Outline

Chapter 1 introduces the fundamental importance of graphene, emphasizing its exceptional properties and its potential for advanced technological applications. It outlines the challenges posed by contamination and structural defects, particularly those introduced during transfer and handling. The research motivation, objectives, and the scope of this thesis are described, establishing the need for developing polymer-free transfer methods and effective in-situ cleaning techniques to produce ultra-clean graphene.

Chapter 2, the literature review, provides an overview of the progress made in the synthesis and transfer of graphene since its discovery. It discusses key techniques such as mechanical exfoliation, chemical vapor deposition (CVD), and epitaxial growth on silicon carbide (SiC), highlighting their strengths and limitations. Particular attention is given to contamination issues arising from polymer-assisted transfers and environmental exposure, as well as previous attempts at cleaning graphene using thermal, chemical, and plasma-based approaches. This chapter identifies the gaps in current methods, thereby setting the stage for the novel approaches developed in this work.

Chapter 3 details the experimental approaches used in the research. It begins with the description of graphene growth via low-pressure and atmospheric pressure CVD on copper substrates and epitaxial growth on SiC. The polymer-free transfer methods

developed in this work are presented in detail, including the preparation of carbon membrane grids and transfer to transmission electron microscopy (TEM) supports. Advanced characterization tools, such as scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and atomic-resolution imaging techniques, are explained, as they form the basis for evaluating the cleanliness and structural integrity of graphene.

Chapter 4 presents the core results of producing ultra-clean suspended graphene. It discusses the limitations of conventional transfer and cleaning methods before introducing the water radiolysis cleaning approach developed in this thesis. Detailed STEM and EELS data are provided to demonstrate the cleanliness and defect-free nature of the graphene achieved through this method. The chapter further discusses the stability of the ultra-clean graphene under high electron doses, the mechanism of hydrocarbon removal by water radicals, and the significance of obtaining large, pristine areas suitable for advanced characterization and device fabrication.

Chapter 5 focuses on the exfoliation and transfer of epitaxial graphene grown on SiC substrates using a polymer-free method, as well as the metal-assisted transfer of CVD-grown graphene. The experimental procedure for exfoliation using Ni/In/Cu stacks is described in detail, followed by the transfer of graphene onto TEM grids and subsequent cleaning. Additionally, this chapter presents the development of a metal-assisted transfer technique using a thin Pd layer to safely transfer CVD-grown graphene onto SiO₂ substrates without direct polymer contact, preserving the pristine graphene surface. Both approaches demonstrate significant improvements in surface cleanliness and structural quality. The chapter presents some of the first atomic-resolution images of transferred

epitaxial graphene and shows that the combination of polymer-free and metal-assisted transfer methods with radiolysis cleaning effectively removes surface contaminants and adlayers. The broader implications for device fabrication, reuse of expensive SiC substrates, and enhancement of graphene's electronic properties are also discussed. Chapter 6 explores the application of ultra-clean graphene as an interfacial layer for remote epitaxy. The methodology for transferring graphene onto GaSb substrates, cleaning the interface in an MBE chamber, and initiating epitaxial growth of Sn layers is presented. This chapter highlights the potential of ultra-clean graphene to enable the detachment of high-quality epitaxial layers for use as flexible and freestanding nanomembranes. The implications for next-generation flexible electronics, optoelectronics, and quantum devices are considered, along with the challenges of maintaining cleanliness outside controlled environments.

CHAPTER TWO

LITERATURE REVIEW

The impurities and defects that arise during the synthesis and transfer of graphene, primarily due to the absence of bulk material, adversely affect its intrinsic properties. This presents a significant challenge when utilizing graphene. Since the groundbreaking discovery of graphene by Andre Geim and Kostya Novoselov in 2004 [1], [2], several processes have been developed to synthesize graphene with fewer impurities and defects. Nevertheless, ongoing experiments aim to maintain the cleanliness and defect-free nature of graphene during its transfer for further applications.

We approached this issue with a straightforward and innovative method designed to minimize contamination and produce ultra-clean, defect-free areas of hundreds of nanometers in size. Due to graphene's two-dimensional structure, traditional cleaning techniques that involve removing sacrificial layers are not applicable. While most inorganic contaminants can be removed using chemicals compatible with graphene, organic contaminants (since they also contain carbon) pose a more significant challenge for removal without damaging the graphene itself. Moreover, graphene has an affinity for organic compounds [3], resulting in the absorption of additional organic molecules from the surrounding environment.

We identified two categories of organic contaminants: those that are strongly bonded and nearly impossible to remove, and those that are loosely bonded. The more resilient organic contaminants often originate from the polymers and solvents used during various processing stages after growth.

In our research, we developed polymer-free methods to transfer CVD-grown graphene

and epitaxial graphene on SiC to TEM grids, allowing for the creation of suspended graphene for further cleaning and characterization. An in-situ cleaning method was employed, which utilized the electron beam of the TEM to produce water radicals from absorbed water molecules on the graphene, effectively removing the remaining organic contaminants. This resulted in ultra-clean areas of graphene, confirmed comprehensively through characterization, each measuring hundreds of nanometers in size.

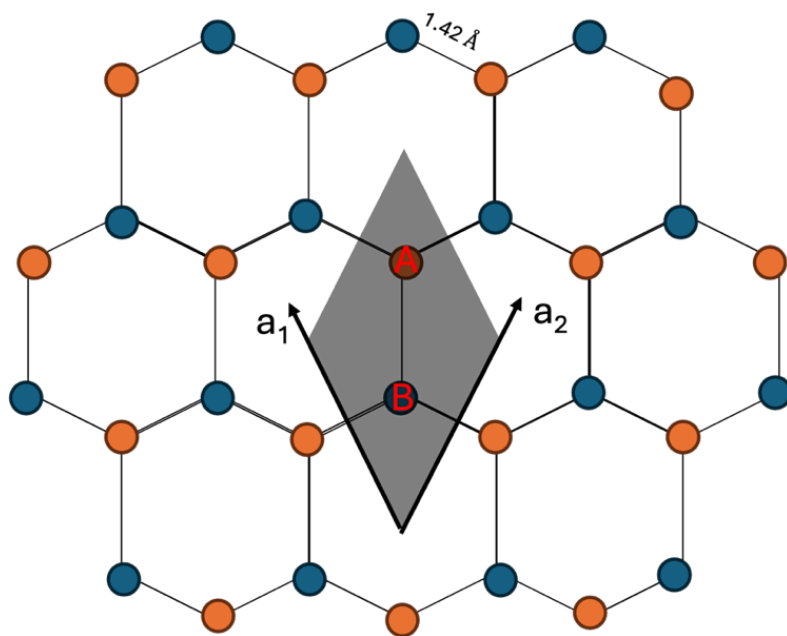


Figure 2.1 The schematic shows the honeycomb structure of graphene. The highlighted area in light grey is the unit cell defined by vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. It contained two atoms in lattice points, A (orange) and B (blue). The length of a single C-C bond is approximately 1.42 Å.

2.1 Graphene Structure and the Importance of Graphene

Graphene, an allotrope of carbon, is a single-layer, 2D material with a honeycomb lattice structure. In this structure, the unit cell consists of two carbon atoms, A and B (refer to **Figure 2.1**). The hexagonal cell is composed of sp^2 hybridized carbon atoms that assemble into a honeycomb pattern. Graphene is considered the fundamental building block of many sp^2 carbon species, including carbon nanotubes, fullerene, and graphite. Renowned as the thinnest material ever created, graphene possesses extraordinary properties, earning it the title 'the material of the century.' A single carbon atom has 4 valence electrons ($1s^2 2s^2 2p^2$). In graphene, C-C bonds are formed by the superposition of $2s$, $2p_x$, and $2p_y$ orbitals, creating stable, localized σ bonds with 3 neighboring carbon atoms in the lattice. These σ bonds primarily contribute to the mechanical properties of graphene [4]. The remaining $2p_z$ orbital forms π bonds, which overlap with neighboring carbon atoms. These π bonds play a significant role in the extraordinary electronic properties of graphene [5].

Charge carriers in graphene have high speeds, around $\sim 10^6 \text{ ms}^{-1}$, and zero rest mass [1]. In this case, electrons are treated as relativistic particles; hence, the Dirac equation for relativistic particles can be applied to explain electron transport. Graphene has a zero-band gap (**Figure 2.2(b)**), and the conductance band and the valence band meet at K-points of the edge of the Brillouin zone (**Figure 2.2(a)**). These points are called 'Dirac points.' The band energy of the graphene is linearly proportional to the wave vector ($\mathbf{k}$) near the Dirac points ($E(\mathbf{k}) \propto k$) due to the relativistic effect on fast charge carriers. Due to this zero-band gap, graphene is categorized as a semimetal or zero-band

semiconductor. Since Andre Geim and Kostya Novoselov first discovered graphene by mechanical

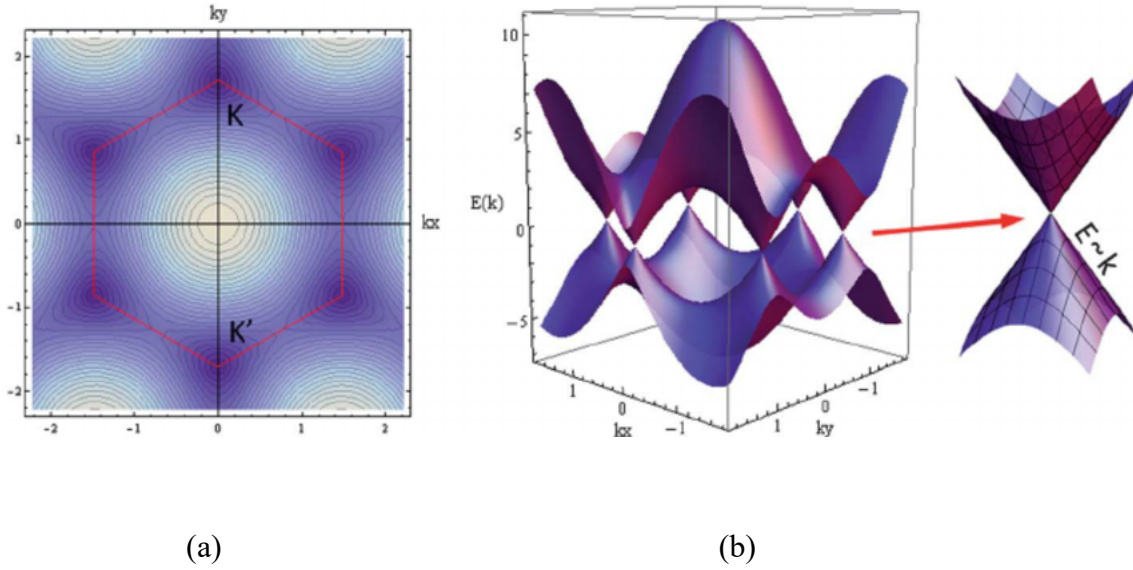


Figure 2.2 (a) A plot of the energy in the first Brillouin zone of graphene (red hexagon). (b) A plot of the band structure of graphene shows the conduction band and the valence band touching at the K points. The zoomed part on the right-hand side shows the linear dispersion in the region of the Dirac points. [6]

exfoliation in 2004, several methods for graphene synthesis have been discovered. The flow chart in **Figure 2.3** gives an overview of graphene synthesis techniques.

2.2 EELS Analysis

In Transmission Electron Microscopy (TEM), a beam of incident electrons interacts elastically and inelastically with the sample. These electrons then scatter through the specimen. Elastically scattered electrons do not lose their energy, resulting in diffraction,

but inelastically scattered electrons lose some of their energy. These loss energies excite the electrons in the specimen. The spectrum of these loss energies is called the electron energy loss spectrum (EELS). The energy loss spectrum can be analyzed by regions based on the energy loss.

01. Zero peak: Unscattered electrons whose energies are not lost. Low loss: ~0-50 eV range. Due to the excitation of the electrons of the atoms in the valence band.
02. Core loss: Above 50 eV. Due to the excitation of the electron from the inner shells of the atoms to the conduction band.

Although few studies have been conducted on the EELS of suspended graphene [7], numerous studies have been conducted on the EELS of graphite [8], [9]. Both graphene and graphite exhibit sp^2 hybridization of carbon, with graphite consisting of multiple layers of graphene. Despite an energy level shift between the monolayer 2D and the bulk layered materials [10], a valid comparison can be made between graphene and graphite (**Figure 2.4**) using core-loss of EELS.

The low-loss region of graphitic carbon mainly comprises plasmon peaks. In graphitic carbon species, we can identify two plasmon peaks.

01. π peak: only π valence electrons are involved in the excitation.
02. $\pi+\sigma$ peak: all valence electrons are involved in the excitation.

The positions of the graphite plasmon peaks depend on the number of graphene layers it consists of [12]. As the number of layers increases, the plasmon peaks shift positively along the energy loss axis, and the areas under peaks also become larger. Since graphene (more specifically suspended graphene. The plasmon peaks of epitaxial graphene exhibit slightly higher energy loss than suspended graphene [12].) has only one layer of carbon

atoms, it experiences the minimum energy loss for both peaks among graphitic species.

(**Figure 2.5**). EELS can effectively separate graphene from other carbon species, so we

utilized EELS analysis in our experiments to produce ultra-clean graphene.

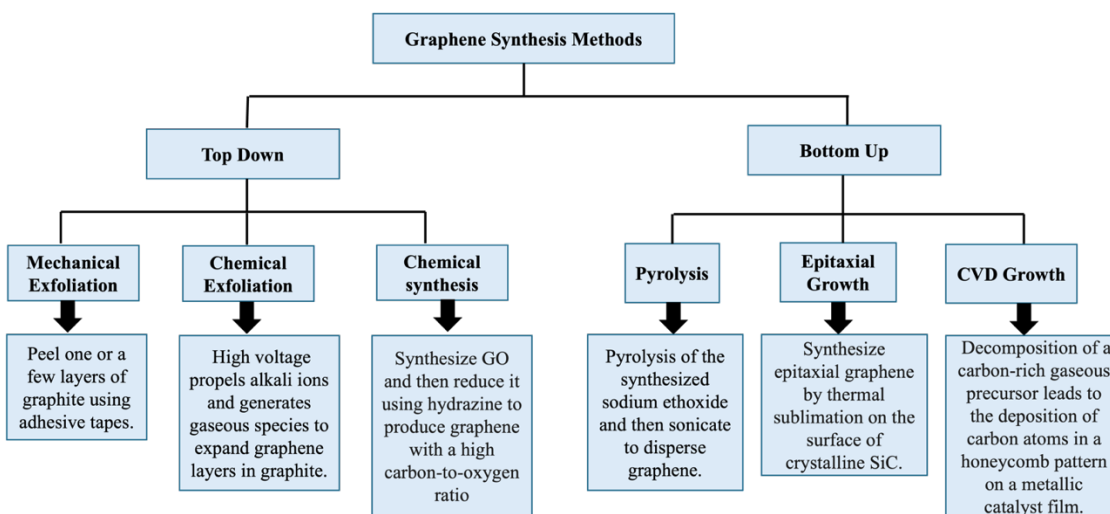


Figure 2.3 An overview of different types of graphene synthesis processes.

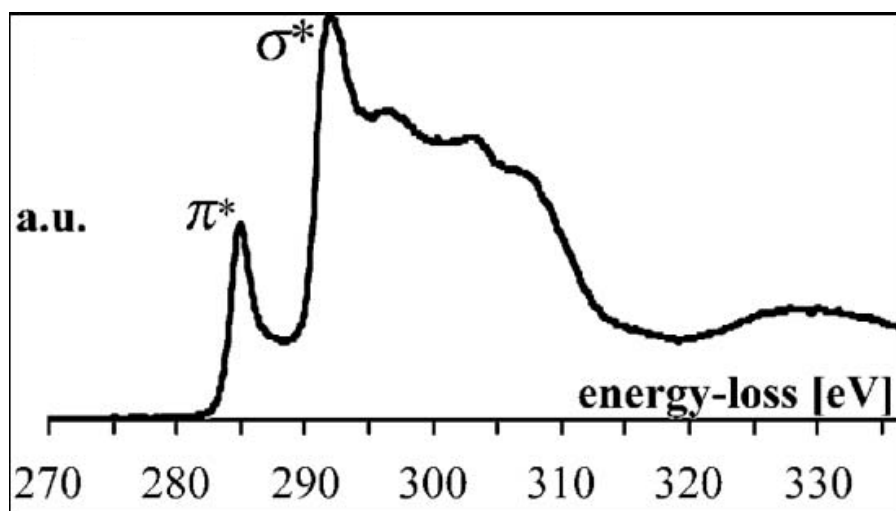


Figure 2.4 Carbon K-edge spectra of graphite [11]. π^* peak caused by electron transition from K-shell to the antibonding state of π bond. σ^* peak caused by the electron transition from K-shell to the antibonding state of σ bond.

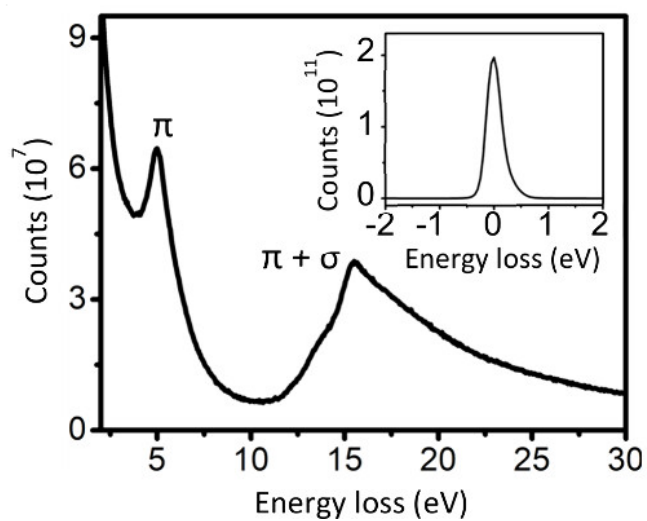


Figure 2.5 Low-loss EEL spectrum of graphene. Inset: Zero-loss peak. [2]

CHAPTER THREE

EXPERIMENTAL TECHNIQUES

3.1 Chemical Vapor Deposition (CVD)

CVD is a deposition method that uses a vacuum to deposit thin films and coatings of various materials. Here, a vapor containing the intended deposition material undergoes a chemical reaction at an elevated temperature and is finally deposited on the given substrate. In graphene grown by CVD, we usually use Cu as the substrate and methane (CH_4) as the vapor species, which carries carbon to grow graphene on the Cu substrate. CVD-grown graphene is known to be the cheapest method to grow large-area monolayer graphene.

In our CVD system in Dr. Gu's lab, we used two different pressure ranges to grow two different types of graphene. One is a low-pressure CVD (LPCVD), which works under a few hundred millitorr pressures. The other one is the atmospheric pressure CVD (APCVD), which works at atmospheric pressure. Using LPCVD, monolayers can be grown on Cu substrates due to the high diffusion coefficient since the process maintains a low pressure. So, the growth will be quick and will cover the entire Cu surface with graphene in a few minutes. Because Cu acts as a catalyst here, once it is covered with the first graphene layer, no more graphene will be grown. Hence, monolayer graphene can be obtained. On the other hand, APCVD showed the ability to grow multilayer graphene [13].

The selection of the Cu substrate is due to the low solubility of carbon species in Cu. Graphite has been grown on Ni substrates in early work [14]. Ni has a high solubility of carbon species, leading to the growth of multiple layers of graphene on the substrate. The

cleaned Cu substrates must be pre-annealed together with H_2 . This step helps to remove the oxide layer from the Cu surface. On the other hand, an elevated temperature (1000 $^{\circ}C$) helps to enlarge the grain sizes of the Cu surface (a few millimeters). In LPCVD, after the annealing, we let the CH_4 gas flow into the quartz tube. CH_4 is catalytically decomposed at an elevated temperature and forms graphene on the Cu surface. Because of the low solubility of carbon in Cu, the growth process stops after the first layer of graphene is formed. In APCVD, due to the low diffusion coefficient, the growth process is slower. Graphene grows slowly around the nucleation center, and carbon species can go underneath the grown graphene. Hence, ad layers can be grown underneath the first layer of graphene. In this way, multilayer graphene islands are grown.

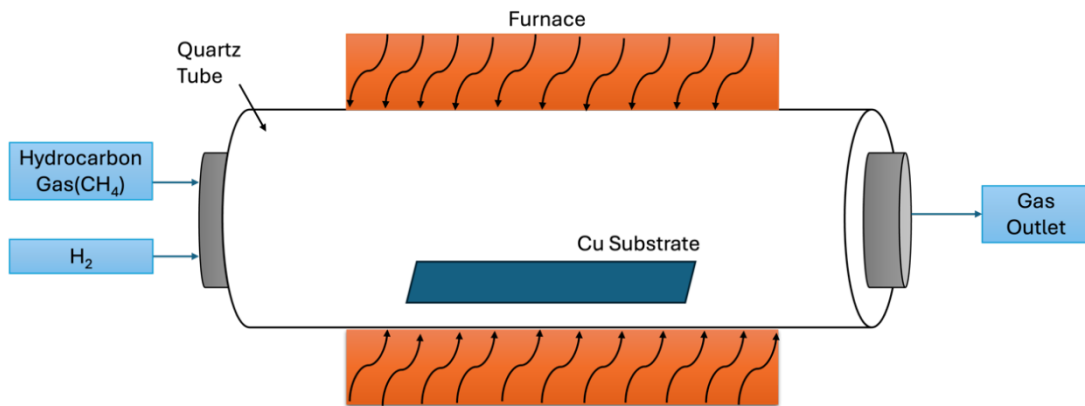


Figure 3.1 Schematic diagram of the CVD system to grow graphene.

CHAPTER FOUR

ULTRA CLEAN SUSPENDED GRAPHENE

Defect-free, high-quality graphene synthesis processes on various substrates have been developed in recent years [15], [16], [17], but very few works have succeeded in defect-free, clean, suspended graphene production. Our group has developed a simple method for producing large-area ultra-clean suspended graphene with no defects [18] from CVD-grown graphene.

4.1 Growing Graphene

We used LPCVD-grown graphene on Cu foil (Alfa Aesar, item No.10950), resulting in a continuous graphene film that completely covers the Cu foil substrate and that is >95% monolayer with small patches of adlayers [17]. Briefly, the copper foil is cleaned by sonication baths in deionized water (DI water), acetone, isopropanol, and a dilute hydrochloric acid solution (5%), each for approximately 5 min. After a DI water rinse, the foil is dried with a nitrogen stream. In a hot wall CVD system (OTF-1200x, MTI corporation), the copper foil is annealed at 1020 °C for 20 min, with a pressure of ~ 100 mTorr sustained by a 25 standard cubic centimeters per minute (sccm) pure hydrogen flow, followed by the 20 min growth initiated by introducing 20 sccm methane to the gas flow and adjust the total pressure to ~280 mTorr. After growth, the sample rapidly cooled down with the gas flows unchanged. The graphene grown in such processes is found to be polycrystalline with boundaries and the mean grain size is about 400 nm [19].

4.2 Transfer of Graphene to the TEM Grid (Direct Transfer)

We use two types of carbon membrane-covered Au grids, Quantifoil (400 mesh) and EMResolution (300 mesh), with periodically arranged regular holes and irregular holes in

the membranes, respectively. The grids are cleaned before use and sequentially immersed in chloroform, acetone, and isopropyl alcohol (2 hours each) at room temperature (RT). After natural drying, the grids are annealed at 900 °C in pure Ar under atmospheric pressure. Graphene is transferred to cleaned grids following the established direct transfer method[20]. The product of the transfer process is known as the sample, with graphene covering the carbon membrane and suspended over the through holes. The sample is pre-cleaned in a tube furnace at 250 °C to 300 °C for 30 min with the quartz tube open to ambient air.

4.3 TEM, STEM, and EELS Acquisition

4.3.1 FEI Spectra 300 MC

FEI Spectra 300 MC is a 300 kV S/TEM equipped with an energy filter and a monochromator, enabling a spatial resolution of ~ 0.5 Å in the STEM mode. Acceleration voltage options include 60, 200, and 300 kV. The energy resolution can reach 200 meV in electron energy-loss spectroscopy (EELS). The sample chamber vacuum is typically about 3×10^{-8} Torr and no worse than 10^{-7} Torr. The EEL spectra in this work were obtained along with atomic-resolution ADF STEM images using Spectra 300 MC, referred to hereafter as Spectra.

4.3.2 Extended Moist Air Exposure

The pre-cleaned sample is placed over DI water (without direct contact) in a covered beaker to ensure sufficiently abundant adsorbed water for the radiolysis cleaning. The moist air exposure is typically overnight, after which the samples are loaded into a TEM. Experiments to reveal mechanisms using dry samples, i.e., those without intentional moist air exposure before loading, are clearly specified.

4.3.3 Electron Shower in Spectra

After an area of interest is quickly located by TEM imaging at an illumination dose rate $< 0.1 \text{ e}^-/(\text{\AA}^2 \text{ s})$, an electron shower is performed. The standard shower in Spectra, using parallel illumination for 30 min at $20 \text{ e}^-/(\text{\AA}^2 \text{ s})$ in a $10 \text{ }\mu\text{m}$ diameter spot, guarantees > 7 hours of continuous STEM operation using an intense focused beam without beam-induced carbon deposition. Varied doses used to explore the process window are clearly specified. The showered area is often subjected to scanning and dwelling-focused beam tests in the STEM mode to verify the elimination of beam-induced carbon deposition. The beam current $\sim 100 \text{ pA}$ focused in a $\sim 1 \text{ }\text{\AA}^2$ spot corresponds to a dose rate of $6 \times 10^8 \text{ e}^-/(\text{\AA}^2 \text{ s})$. The dwelling time for the dwelling beam test is 1 min.

4.4 Characterization using STEM imaging and EELS Mappings

The Transmission Electron Microscope (TEM) plays a crucial role in the analysis of 2D materials. Extensive research has focused on obtaining atomic-resolution images of graphene [21], [22]. Only a small, clean area of a few nanometers is required to capture such images. However, achieving a large, clean area of graphene ($\sim 100 \text{ nm}$) has been challenging due to contaminants introduced at various stages of graphene handling. These contaminants have raised concerns about the existence of truly free-standing graphene. As a result, acquiring high-quality Electron Energy Loss Spectra (EELS) of graphene comparable to graphite has been hindered by these contaminants, making it difficult to compare graphene's chemical bonding and band structure with graphite. In our work, we have achieved ultra-clean graphene and obtained EEL spectra of graphene relevant to the chemical bonding and band structure, which nobody has obtained before. Our method is

simple, robust, and repeatable.

The core-loss spectrum demonstrates a high signal-to-background ratio, indicating exceptional cleanliness, as contaminants contribute to the background signals. In **Figure 4.1(a)**, we compared our raw data with a graphite C-K edge spectrum [8]. Here, we labeled Energy Loss Near Edge Structures (ELNES) peaks as A, B, C, etc. A represents the π^* (anti-bond state of π) peak, and B, C, etc., denote the delicate features of the broader σ^* (anti-bond state of σ) peak. In our work, the separation between peaks B and C is unprecedentedly resolved. Graphite is bulkier compared to graphene, a single atomic layer. Obtaining ELNES is much easier for graphite as bulk dominates over the surface. The atomic resolution image with a defect less honeycomb structure in **Figure 4.1(a)** proves that our graphene is a single atomic layer. Therefore, cleanliness is crucial to resolve fine features in ELNES. Large clean areas are more important than a few nanometer-sized clean windows. **Figure 4.1(c)** shows clean (dark) regions hundreds of nanometers in linear dimensions with traces of solidified contaminants (gray) in between. Also acquired with an unusually high dose, the raw low-loss EEL spectrum (**Figure 4.1(b)**) clearly reveals the π and $\pi + \sigma$ plasmon peaks at 5.1 and 15.5 eV, respectively, modifying the earliest reported values (4.7 and 14.5 eV) extracted from noisy data [22], [23] and slightly updating or validating more recent results (4.90 and 15.4 eV) [24]. The method for achieving ultra-cleanness is simple and robust. As explained in sections **4.1** and **4.2**, the prepared sample is exposed to air of near-saturation humidity overnight. After sample insertion to the TEM chamber, an electron shower is applied, with a parallel broad beam (typically 10 μm diameter) at 20 $\text{e}^-/(\text{\AA}^2\text{s})$ for 30 min, resulting in a level of cleanness that allows continuous operation of a very intense STEM probe for an entire

workday without carbon deposition. The shower time and beam intensity can vary in large ranges. A sufficiently energetic electron beam can form radicals out of water. These radicals can be used to remove hydrocarbons by forming volatile products. Organic contamination is currently a significant obstacle in achieving ultra-clean graphene. We have successfully demonstrated the utility of water radicals formed by electron beams by exposing electron beams to water-absorbed contaminated graphene. When the electron beam is showered on hydrocarbons, radiolysis causes carbonation (traces in **Figure 4.1(c)**). Visible contaminants are formed, which are tough to remove. As we perform overnight water absorption, absorbed water undergoes water hydrolysis and forms water radicals. These radicals react with hydrocarbon contaminants and remove them by forming volatile products. When there is sufficient water absorption on graphene, effective cleaning will occur by overtaking carbonization. Due to the significant difference in chemical stability between graphene and organic contaminants, water radiolysis products effectively remove hydrocarbons without disturbing the graphene. After subjecting clean graphene areas to an electron shower, we observed zero defects, as shown in **Figure 3.1(a)**, indicating that pristine graphene is stable and robust.

4.5 Obstacles and Future Improvements

We have plenty of opportunities to improve the process we have developed. For instance, we can reduce the formation of irremovable graphitic residues during precleaning by lowering the thermal oxidation temperature. Another option is deliberately introducing organic adsorbates with groups such as -OH and -CO to promote radiolysis reactions that produce volatile products. The process we developed was only experimented inside the TEM chamber under a vacuum. Once the clean areas are exposed to the environment, the

attraction of hydrocarbon makes the clean areas dirty again. So, to make this discovery useful and applicable, it is essential to keep the clean for longer in normal conditions. We are continuously working on improving the process and have already begun using it for other graphene applications.

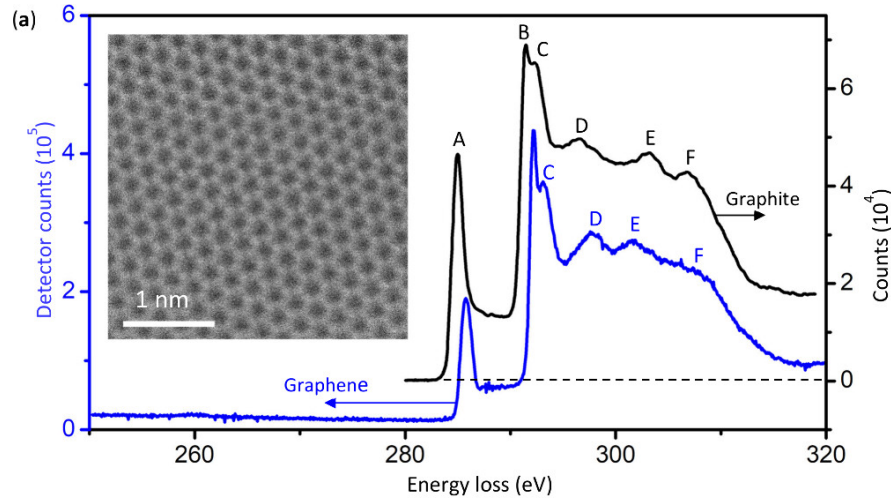


Figure 4.1 EEL spectra and STEM images of ultraclean graphene. Only raw data are shown in the main text to showcase data quality. (a) Core-loss spectrum of ultraclean graphene (in detector counts) in comparison with that of graphite [8], each with zero count level indicated even though the latter is background-subtracted. For our graphene spectrum, ~ 16 detector counts represent one detected electron, therefore each analyzer channel in the C-K spectral range detects a high electron count in the order of 10^4 . This raw spectrum is compared to energy resolution-sharpened ELNES of graphite [25], analyzed to reveal peak positions and widths, and compared with state-of-the-art graphene core-loss spectrum raw data [7]. Inset: Atomically resolved ADF STEM image acquired at 60 kV with high beam current (111 pA) and long exposure (11.5 min). (b) Low-loss EEL spectrum. Inset: Zero-loss peak. (c) Overview ADF STEM image acquired at 200 kV showing large clean areas with traces of solidified contaminants.

CHAPTER FIVE

METAL-ASSISTED TRANSFER OF EPITAXIAL GRAPHENE GROWN ON SILICON CARBIDE (SiC) AND CVD-GROWN GRAPHENE

5.1 Metal-Assisted Transfer of Epitaxial Graphene Grown on SiC

Badami first demonstrated graphitization of the surface of a SiC single crystal in 1965 [26]. In 2008, it was found that homogeneous graphene growth is possible by annealing SiC single crystals in an Ar atmosphere [27], [28]. Since then, this procedure has been developed, and now one can obtain homogenous monolayer, bilayer, etc. graphene on SiC (0001) face.

Graphene can be grown on SiC on two faces: C-face (000 $\bar{1}$) and Si-face (0001) (**Figure 5.1**). In C-face, growing graphene is less controllable, and multilayers of graphene will be grown due to the higher reactivity of the carbon layer. On the other hand, Si-face has better control over growing homogeneous graphene. Single, bilayer, and few-layer graphene can be grown on the Si face by controlling the heating temperature.

In the process of growing graphene on silicon carbide (SiC), the substrate is heated to high temperatures, typically between 1200 and 1600 °C, in a vacuum or an inert gas atmosphere, such as argon. At these elevated temperatures, silicon atoms start to evaporate from the surface of the SiC substrate. This is a critical step, as the silicon atoms exit the crystal lattice. As silicon is removed, the remaining carbon atoms on the surface rearrange and bond together, forming graphene layers. By controlling the temperature and duration of this process, one can manipulate the number of graphene layers produced. Generally, higher temperatures and longer processing times result in thicker graphene films.

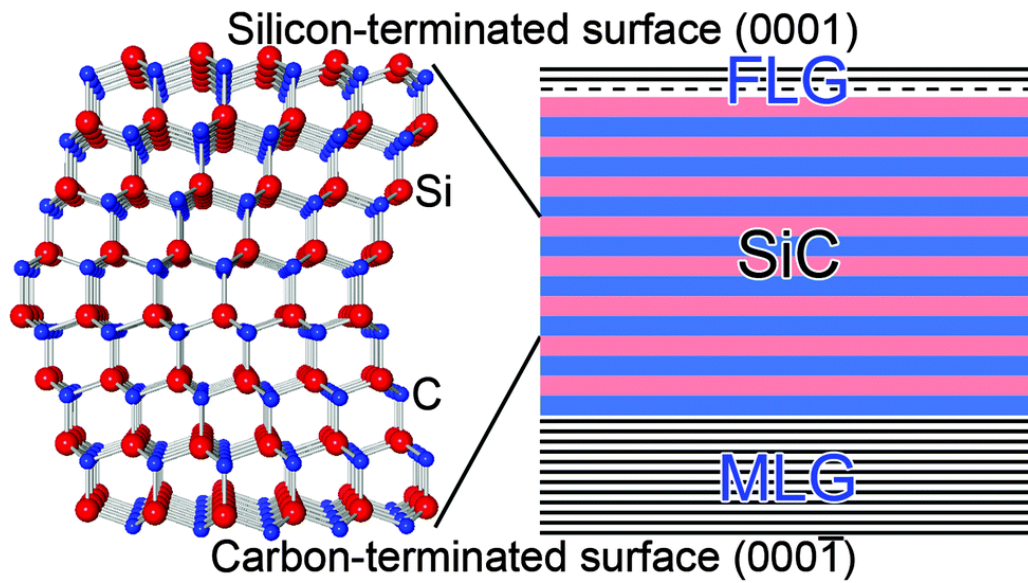


Figure 5.1 Crystal structure of 6H-SiC and an illustration of graphene on its surfaces. The large, red, and small blue balls correspond to the silicon and carbon atoms, respectively. On the Si-terminated (0001) face, few-layer graphene (FLG) grows, and on the C-face (000 $\bar{1}$), multi-layer graphene (MLG) grows [29].

SiC-grown graphene has some unique features compared to other types of graphene. Epitaxial graphene grown on SiC has high-quality crystal structure without grain boundaries. Hence, single crystal graphene sheets as large as SiC substrate can be obtained. Almost all the SiC-based devices were fabricated on the SiC substrates without transferring them to another substrate.

The properties of graphene transferred from SiC have not been fully understood. Previous methods for transferring graphene from SiC have involved polymer-based transfers, which can introduce irremovable organic contaminants to the graphene.

Although single-layer graphene can be grown on the Si-face by controlling the temperature, ad-layer stripes can form underneath the single layer, impacting its properties. Epitaxial growth of graphene follows the step edges of the SiC substrate, and the formation of a carbon buffer layer (which is not graphene) right above the SiC layer can pose challenges and reduce quality when fabricating devices on the graphene on SiC substrate. Additionally, single crystal SiC substrates are expensive, so reusing the SiC substrate for another graphene growth is feasible if the grown graphene is transferred. To address these, we have developed a polymer-free transfer method that allows for the transfer of graphene from SiC to various substrates, such as Si/SiO₂ substrates and TEM grids (suspended graphene).

5.2 Preparation of the Carbon Membrane of the TEM Grid for the Transfer

We use two types of carbon membrane-covered Au grids, one of which is Quantifoil (400 mesh), which has periodically arranged regular holes, and the other one is EMResolution (300 mesh), which has randomly scattered irregular holes in the carbon membrane. The grids are annealed for 30 minutes at 900 °C in pure Ar under atmospheric pressure. Then, the carbon membrane is detached from the gold frame by electrolysis. KOH solution (2 mol/dm³) is used as the electrolyte, and a piece of W film (Alfa Aesar, product no: 10417, 50 μm thick) and the grid are used as the anode and the cathode, respectively. The partially detached carbon membrane is removed from the KOH solution and released into a fresh deionized water (DI water) beaker. Then, the floating carbon membrane on DI

water is scooped using a magic loop (Electron Microscopy Sciences, product no: 70740) and released into another fresh DI water beaker. Finally, the carbon membrane is cleaned by repeating this process 3 - 4 times.

5.3 Exfoliation of Epitaxial Graphene from SiC Substrate

Epitaxial graphene grown on the Si face of 6H-SiC via thermal deposition of rectangular-shaped (0.5cmx1cm) SiC samples in an Ar atmosphere were received from Penn. State University. 260 nm thick Ni films were deposited on top of the graphene layers.

O₂ plasma treatment is done on the sample for 5 minutes in a plasma cleaner (Harrick Plasma PDC32G). A rectangular-shaped piece of Cu film (NILACO, 80 μ m thick) and a piece of Indium (In) - ribbon (Chip Quik, SMDIN100-R) are cleaned separately by sonication baths in DI water, acetone and isopropanol, and they are blown dried using an N₂ gun. The film is put on top of the Cu film and heated at around 150 °C until the In film starts melting on the Cu film. Melting In film is scraped until the In film becomes shiny. The Cu/In stack is let to cool down, then dipped in dil. HCL, washed in DI water, and finally, blown dried using an N₂ gun.

A Cu/In stack is kept on the SiC sample (fig.1(b)), and the stack is rolled down a few times using the cylindrical face of a glass block to ensure that In is well attached to the whole Ni film. Finally, the whole stack (SiC on the bottom) is baked at 120 °C on a hot plate for 5 minutes while being pressed by putting a weight on it. The graphene/Ni/In/Cu stack is easily picked up from the SiC substrate.

5.4 Transfer of Exfoliated Graphene into TEM Grid

A previously detached and cleaned carbon membrane is scooped by the graphene/Ni/In/Cu stack. A glass pipet is used to drop 1-2 drops of isopropanol on the

scooped carbon membrane. The stack is left to dry naturally; it is baked at 120 °C for 10 minutes afterward. Then the stack is put into FeCl_3 : HCl (< 1%, HCl) and left it 2hrs to etch away Ni/In/Cu. The magic loop or a flat Au grid (without the carbon membrane) is used to scoop the graphene/carbon membrane from the FeCl_3 : HCl solution and washed with DI water several times (as discussed above). Finally, the graphene/carbon membrane stack is scooped with an Au grid and left naturally dry. Finally, transferred graphene on the TEM grid is baked at 120 °C for 10 minutes. We utilize two types of carbon membrane-covered Au grids.

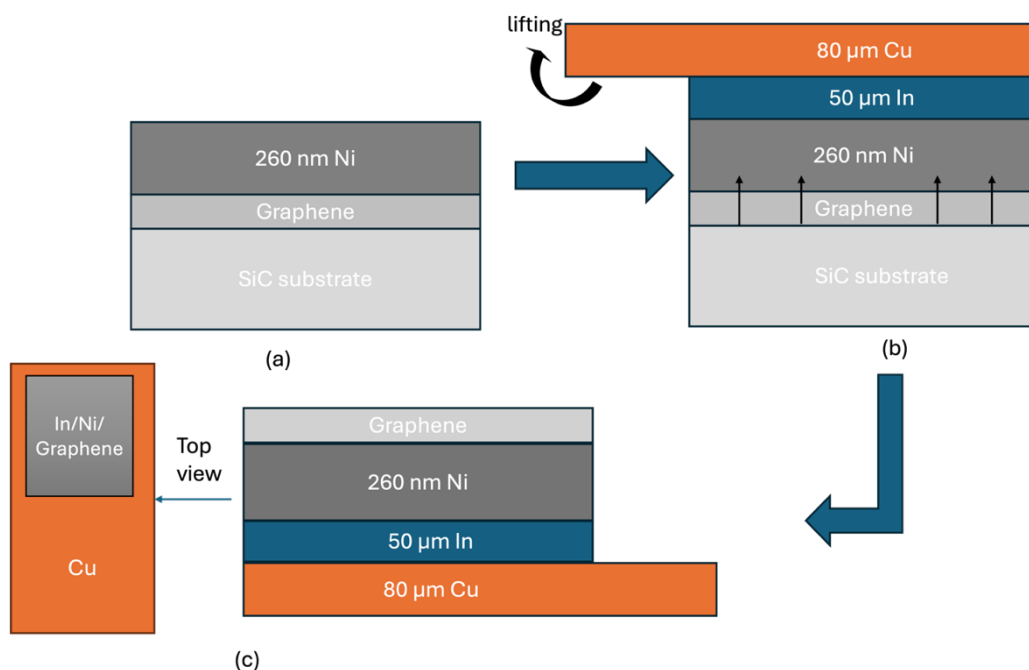


Figure 5.2 Exfoliation of graphene from SiC; (a) O_2 plasma is done on the Ni Surface, (b) stack of Cu-handle and In-tape is attached to the Ni surface, (c) exfoliated graphene/Ni onto the Cu/In stack.

The first type is the Quantifoil (400 mesh), which has regularly arranged holes; the second type is the EMResolution (300 mesh), which features randomly scattered irregular holes in the carbon membrane. The grids are annealed for 30 minutes at 900 °C in pure Ar under atmospheric pressure. The carbon membrane is detached from the gold frame through electrolysis. We use KOH solution (2 mol/dm³) as the electrolyte, with a piece of W film (Alfa Aesar, product no: 10417, 50 µm thick) serving as the anode and the grid as the cathode. The partially detached carbon membrane is removed from the KOH solution and transferred to a fresh deionized water (DI water) beaker. Subsequently, the floating carbon membrane in DI water is scooped using a magic loop (Electron Microscopy Sciences, product no: 70740) and transferred to another fresh DI water beaker. Finally, the carbon membrane is cleaned by repeating this process 3 - 4 times.

The process involves growing epitaxial graphene on the Si face of 6H-SiC by thermally depositing rectangular-shaped (0.5 cm x 1 cm) SiC samples in an Ar atmosphere. The samples were obtained from Penn State University. 260 nm thick Ni films were deposited on the graphene layers after graphene growth. In our lab, the sample underwent O₂ plasma treatment for 5 minutes in a plasma cleaner (Harrick Plasma PDC32G). A rectangular-shaped piece of Cu film (NILACO, 80 µm thick) and a piece of In ribbon (Chip Quik, SMDIN100-R) are separately cleaned by sonication baths in DI water, acetone, and isopropanol. They are then dried using an N₂ gun. The In film is placed on top of the Cu film and heated at around 150 °C until the In film starts melting into the Cu film. The melted In film is scraped until it becomes shiny. The Cu/In stack is then cooled down, dipped in dilute HCl, washed in DI water, and dried using an N₂ gun. Cu/In stack is placed on the SiC sample (fig.1(b)), and the stack is rolled down a few times using the cylindrical

face of a glass block to ensure that the In is well attached to the whole Ni film. Finally, the whole stack (SiC on the bottom) is baked at 120 °C on a hot plate for 5 minutes while pressed using a cylindrical glass block. The graphene/Ni/In/Cu stack is easily picked up from the SiC substrate.

The process is started by scooping the previously detached and cleaned carbon membrane using the graphene/Ni/In/Cu stack. Next, 1 - 2 drops of isopropanol are dropped on the scooped carbon membrane using a glass pipette. The stack is left to dry naturally and baked at 120 °C for 10 minutes. Afterward, the stack is placed into FeCl₃ : HCl solution (with HCl concentration less than 1%) and left for 2 hours to etch away Ni/In/Cu. The graphene/carbon membrane is then scooped from the solution using a magic loop or a flat Au grid (without the carbon membrane) and washed with DI water several times. Finally, the graphene/carbon membrane stack is scooped with an Au grid, left to dry naturally, and baked at 120°C for 10 minutes.

5.5 Characterization Using STEM Imaging and EELS Mapping

STEM imaging and EELS analysis, as outlined in section 5.3, have also been utilized to characterize the transferred epitaxial graphene grown on SiC. We were able to capture what is likely the best raw image ever taken of graphene (see **Figure 5.3(a)**). This image marks the first instance of atomic-resolution imaging of epitaxial graphene (EG) transferred from SiC. The quality of these results can be attributed to the graphene's exceptional cleanliness. As described in the methodology, we employed a polymer-free transfer method to move the graphene from SiC, thereby avoiding the introduction of tough organic contaminants that typically arise from polymer-assisted methods. Consequently, our graphene initially exhibits significantly lower levels of organic contamination.

Despite the reduction in contaminants, the attraction of hydrocarbons from the surrounding environment remains unavoidable. After transferring the EG onto the TEM grid, we performed thermal annealing at a controlled temperature range of 250-300 °C in ambient air to further diminish contaminants. As mentioned in section 3, the water radiolysis method was employed as the critical final cleaning step to ensure we achieved pristine graphene by eliminating hydrocarbon residues.

The low-loss region of the acquired EEL spectrum (**Figure 5.1(c)**) reaffirms the plasmon peak values previously noted in section 3 for transferred CVD-grown graphene. The π and $\pi+\sigma$ peak values are observed at 5.0 eV and 15.5 eV, respectively (the values reported in section 3 are 5.1 eV and 15.5 eV). The core-loss spectrum shows a high signal-to-background ratio, indicative of outstanding cleanliness, as contaminants typically contribute to the background signals (**Figure 5.1(b)**). Similar to the core loss of CVD-grown transferred graphene, the separation between peaks B and C has been resolved for the first time for EG graphene transferred from SiC.

5.6 Adlayer Removal from the SiC-grown Graphene

There are two reasons for the adlayer growth of the graphene on SiC.

1. Adlayers are growing underneath the graphene monolayer due to the carbon atoms presented on the SiC substrate.
2. Due to the carbon species presented on the growing chamber, on the top of the monolayer graphene, ad layers can be formed.

One of the samples we got from the NIST (National Institute of Standard and Technology) has an ad layer of graphene growth on the top of the mono-layer graphene (due to the

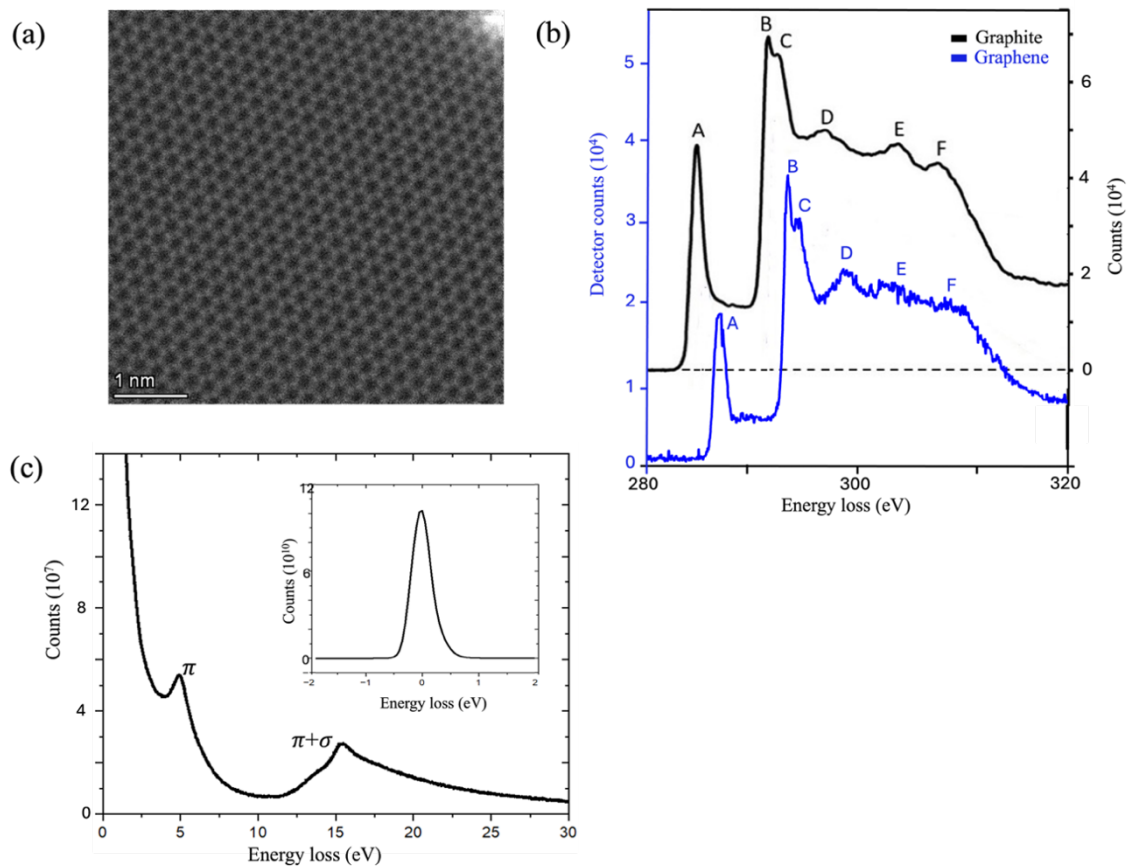


Figure 5.3 EEL spectra and STEM images of ultraclean graphene. Only raw data are shown in the main text to showcase data quality. (a) Core-loss spectrum of ultraclean graphene (in detector counts) in comparison with that of graphite [8], each with zero count level indicated even though the latter is background-subtracted. For our graphene spectrum, ~ 16 detector counts represent one detected electron, therefore each analyzer channel in the C-K spectral range detects a high electron count in the order of 10^4 . This raw spectrum is compared to energy resolution-sharpened ELNES of graphite [25], analyzed to reveal peak positions and widths, and compared with state-of-the-art graphene core-loss spectrum raw data [7]. Inset: Atomically resolved ADF STEM image acquired at 60 kV with high beam current (111 pA) and long exposure (11.5 min). (b) Low-loss EEL spectrum. Inset: Zero-loss peak. (c) Overview ADF STEM image acquired at 200 kV showing large clean areas with traces of solidified contaminants.

carbon species present in the chamber), which needs to be removed to get the optimum results after making a device. We showed that by doing metal-assisted transfer, the adlayers can be removed as well. And proved these adlayers are grown on top of the graphene layer and not because of the C atoms on the substrate (adlayers grown on the bottom of the graphene monolayer) but carbon species present inside the chamber environment. We transferred graphene layer grown on SiC onto a Si/SiO₂ substrate and did AFM imaging before and after transfer and shown that the adlayers are really removed by the metal layer.

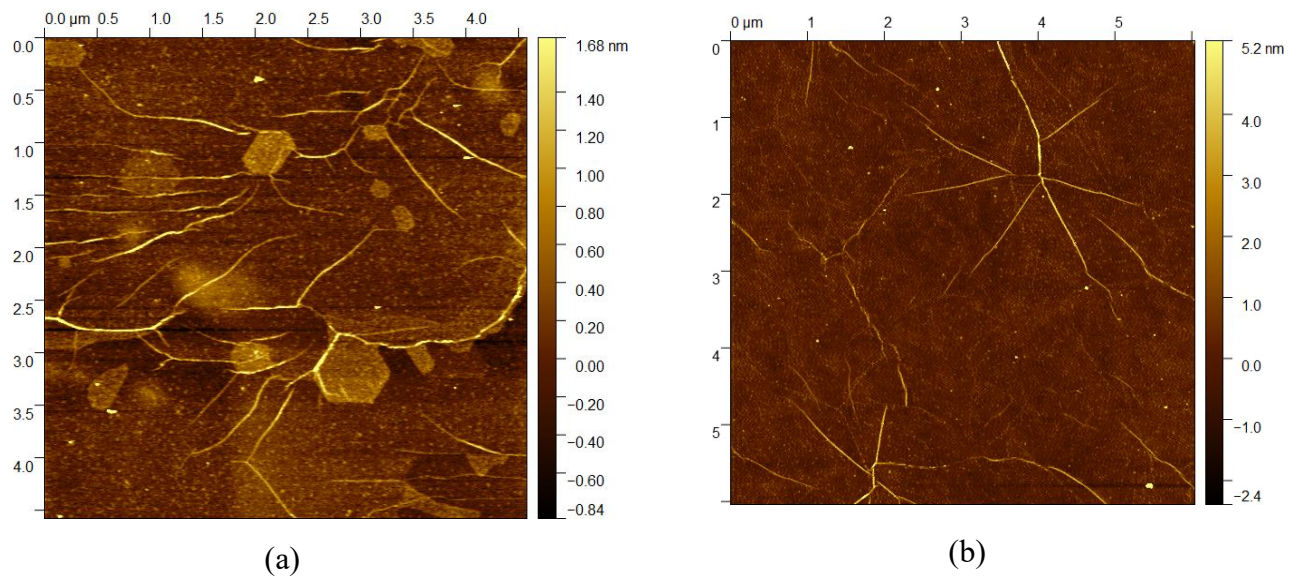


Figure 5.3 AFM height image of (a) graphene on SiC, (b) Graphene transferred to Si/SiO₂ from SiC.

5.6.1 Metal-Assisted Transfer of SiC-Grown Graphene onto SiO₂ Substrates

Following the successful exfoliation of epitaxial graphene from SiC using the Ni/In/Cu stack, the same metal-assisted approach was applied to transfer the graphene onto Si/SiO₂ substrates. This method enables direct transfer without the use of polymers, ensuring a clean graphene surface ideal for electronic and optical characterization.

After exfoliation, the graphene/Ni/In/Cu stack was floated on the surface of deionized (DI) water. A freshly cleaned Si/SiO₂ substrate (300 nm SiO₂ on Si) was prepared by sequential sonication in acetone, isopropanol, and DI water for 10 minutes each, followed by N₂ drying and surface activation by O₂ plasma. The floating graphene/Ni/In/Cu film was carefully scooped onto the Si/SiO₂ substrate with the Cu side facing upward. A few drops of isopropanol were added to enhance surface contact and remove trapped air bubbles. The sample was allowed to dry naturally for 20 minutes and baked at 120 °C for 10 minutes to improve adhesion and remove moisture. The metal layers were then sequentially removed by immersing the sample in FeCl₃ : HCl (<1% HCl) for approximately 2 hours to etch Ni, In, and Cu. The sample was subsequently rinsed in DI water several times and dried using an N₂ gun. Finally, the transferred graphene on SiO₂ was baked again at 120 °C for 10 minutes.

This polymer-free metal-assisted transfer process resulted in uniform, wrinkle-free graphene films on SiO₂ with minimal contamination compared to conventional PMMA-assisted methods. AFM further characterized the transferred samples to examine the surface morphology and verify adlayer removal during the transfer process (Figure 5.4).

5.6.2 Atomic Force Microscopy (AFM) Characterization

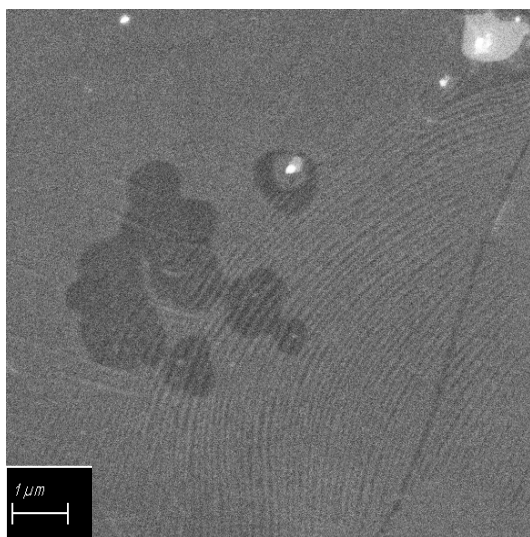
The surface morphology of SiC-grown graphene before and after metal-assisted transfer onto SiO₂ was analyzed using an Oxford Instruments AFM system operating in tapping mode under ambient conditions. AFM images were collected over scan areas of 5 μm $\times$ 5 μm to assess the topography and adlayer features. Before transfer, the SiC-grown graphene exhibited clear adlayer regions appearing as elevated islands with height variations between 0.35 nm and 0.5 nm relative to the monolayer surface. These features arise from excess carbon species during epitaxial growth, which form additional graphene layers above the monolayer. After metal-assisted transfer, AFM images revealed a significant reduction in adlayer features. The transferred graphene displayed a smooth and uniform morphology with an RMS roughness of approximately 0.2 nm over 5 μm $\times$ 5 μm scan areas. The absence of adlayer islands confirms that the adlayers were located above the monolayer graphene and were effectively removed during the transfer, as they adhered to the Ni film and were etched away with the metal layers.

These AFM results confirm that the metal-assisted transfer method not only achieves polymer-free transfer but also acts as an effective adlayer-removal process for epitaxial graphene grown on SiC.

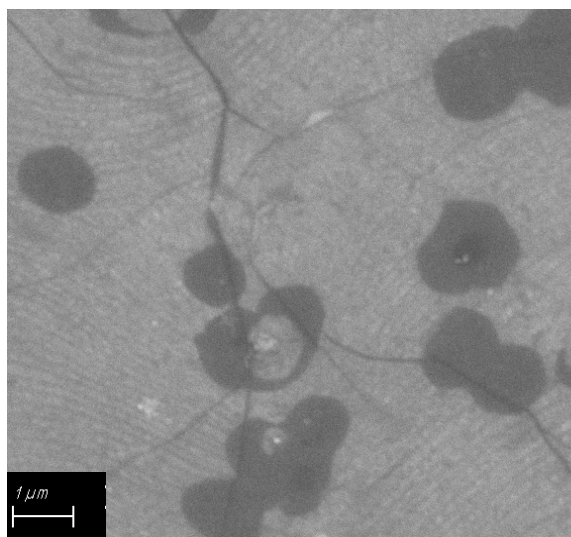
5.7 Metal-assisted transfer of CVD-grown graphene

Up to now, we have used the metal-assisted transfer only on SiC-grown graphene. But for the CVD-grown graphene, we attempted the same process by depositing a Palladium (Pd) layer by e-beam evaporation on graphene and successfully transferred the graphene onto SiO₂. We did Optical and SEM imaging on this, and we are hoping to do further characterizations in the future.

Here, I deliberately used an adlayer-rich graphene to observe any adlayer removal by the metal film, as we observed in SiC Graphene. But we have not seen any adlayer being removed. The adlayer in CVD graphene growth grows underneath the monolayer. So, the deposited Pd layer will not pick up the adlayers.



(a)



(b)

Figure 5.5 SEM image of (a) Graphene on Cu after growth by CVD. (b) The same graphene as (a) was transferred onto Si/SiO₂ by metal-assisted transfer

5.7.1 Graphene Growth on Cu Substrates

Graphene was synthesized on copper (Cu) substrates via low-pressure chemical vapor deposition (LPCVD). Commercially available AA 10950 Cu foils were used as the catalytic substrate. Before growth, the Cu foils were cleaned using acetone, isopropanol, and deionized (DI) water, followed by drying with nitrogen gas. After graphene growth, a 50 nm palladium (Pd) layer was deposited onto the graphene surface using the thermal evaporation method. The Pd layer served as a mechanical support and protective interlayer during the subsequent transfer process, effectively isolating the graphene from direct chemical or polymer contact.

5.7.2 Metal-Assisted Graphene Transfer Procedure

A metal-assisted transfer method was developed to safely transfer the graphene layer onto a SiO₂ substrate without exposing the graphene surface to polymers or corrosive etchants. The detailed steps are described below.

(a) Backside Cleaning and Flattening

A 1 cm × 1 cm Pd-deposited Cu/graphene sample was prepared. The backside of the Cu foil was treated with O₂ plasma at a high-power setting for 1 minute to remove any residual carbon contamination and enhance wettability. The treated sample was then gently flattened by placing it between two larger Cu foil pieces and pressing it with a cleaned glass slide to ensure uniform flatness.

(b) PMMA Coating (Support Layer Preparation)

A thin PMMA support layer was spin-coated on top of the Pd surface and baked at 100 °C for 10 minutes to improve adhesion and remove solvent residues. Importantly, PMMA never came into direct contact with graphene, as the Pd layer served as an intermediate buffer, preserving the pristine graphene surface. A 4 mm × 4 mm square region was then cut from the center of the coated area using a fresh blade and a cleaned glass slide as a straight edge.

(c) Cu Foil Etching

The PMMA/Pd/graphene/Cu stack was floated on a freshly prepared 0.2 M ammonium persulfate (APS) solution for 3 hours to completely remove the Cu substrate. After Cu dissolution, a PMMA/Pd/graphene film remained floating on the surface of the etchant.

(d) Transfer onto SiO₂ Substrate

The floating PMMA/Pd/graphene film was carefully transferred onto a SiO₂ piece that had been sequentially wet cleaned and O₂ plasma cleaned immediately before use. The film was rinsed with DI water multiple times to remove APS residues and then transferred onto a fresh SiO₂ substrate. The transferred sample was allowed to air dry for 1 hour, followed by gradual heating to 120 °C for 20 minutes on a hot plate. The temperature was increased and decreased slowly to prevent stress-induced wrinkling or film damage.

(e) PMMA Removal and Pd Surface Cleaning

The PMMA support layer was removed by immersing the sample in acetone for 1 minute, followed by transfer to a fresh acetone bath for 3 hours to ensure complete dissolution. The sample was then rinsed with isopropyl alcohol (IPA) and dried under a nitrogen stream.

To remove trace PMMA residues remaining on the Pd surface, the sample was treated with UV/O₃ for 10 minutes.

(f) Pd Etching and Graphene Cleaning

The Pd layer was subsequently removed using a commercial FeCl₃/HCl solution (diluted with water at 4 : 1) for 1 hour. The sample was thoroughly rinsed with DI water, then immersed in dilute aqua regia (AR : water = 1 : 4) for 30 minutes to remove any residual metallic contaminants. After cleaning, the sample was again rinsed with DI water and dried at 40 °C to remove surface moisture. Once no visible water remained, the sample was heated at 100 °C for 5 minutes to complete the drying process and stabilize the transferred graphene layer.

5.7.3 Summary

This metal-assisted graphene transfer method enables the safe and clean transfer of graphene from Cu to SiO₂ substrates without direct polymer or chemical contact with the graphene surface. The Pd interlayer provides both mechanical stability and chemical protection throughout the process, preventing graphene etching or contamination

typically observed in polymer-assisted transfers. The inclusion of UV/O₃ cleaning and acidic metal-removal steps ensures minimal residue and yields high-quality, contamination-free graphene suitable for further epitaxial growth or electronic characterization.

5.8 Adlayer-free graphene growth by CVD

As explained at the beginning, the adlayers were grown on the bottom of the monolayer graphene; due to the uncontrolled nucleation, we cannot remove them by removing the Pd metal film. We were able to grow an ad-layer-free graphene (Figure 5.7) primarily based on previous works [17]. So, in the future, we can use an ad-layer-free graphene combined with metal-assisted transfer for projects like remote epitaxy.

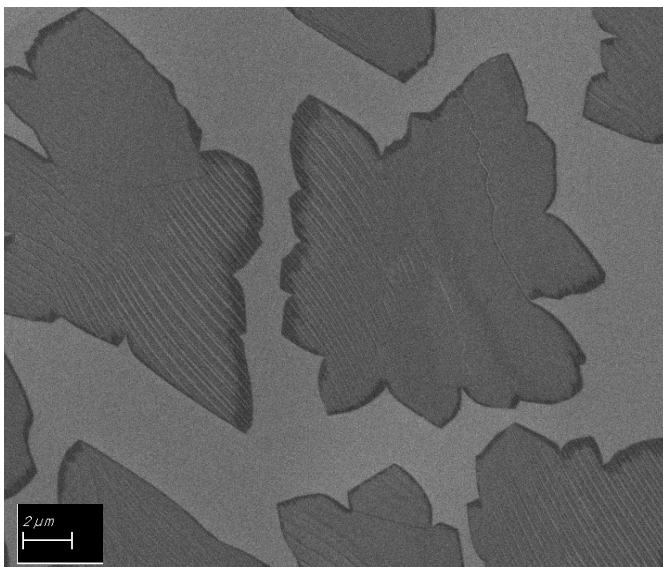


Figure 5.5 SEM image of adlayer-free graphene islands growth on Cu by the CVD method.

5.9 Future Work

In this work, we have developed a polymer-free method to transfer epitaxial graphene (EG) from SiC. Our next step is to apply and optimize this transfer technique for practical applications. We plan to conduct electrical transport measurements on the transferred graphene by placing it on various substrates to investigate potential improvements in its electronic performance. While numerous devices have been fabricated using EG directly on SiC, very few successful demonstrations exist for transferred EG, particularly those avoiding polymer contamination. Maintaining graphene's cleanliness during device fabrication remains one of the primary challenges, and our method provides a promising route to overcome this limitation.

Furthermore, for metal-assisted transfer, we aim to explore the possibility of transferring graphene onto TEM grids for detailed structural and compositional characterization. To the best of our knowledge, metal-assisted transfer of CVD-grown graphene has not yet been reported. Building on this approach, we also plan to fabricate Hall devices to perform further electrical measurements and evaluate carrier mobility and uniformity. In the long term, this polymer-free, metal-assisted transfer method could be extended and adapted for advanced applications such as remote epitaxy.

CHAPTER SIX

APPLICATION OF ULTRACLEAN GRAPHENE- REMOTE EPITAXY

6.1 Introduction

Epitaxy refers to the process of growing crystalline layers with specific orientations relative to an underlying seed crystal. The resulting film, known as the epitaxial layer, inherits the lattice structure and orientation of the substrate, enabling the fabrication of high-quality crystalline materials essential for advanced semiconductor devices. Epitaxial growth plays a central role in producing materials with superior electronic and optical properties, facilitating the development of high-performance transistors, lasers, and photodetectors [31]. However, a major limitation of conventional epitaxy is the strong bonding between the epitaxial layer and its substrate, which prevents detachment after growth. Consequently, the expensive or lattice-matched substrate can only be used once, significantly increasing production costs and limiting device design flexibility.

To overcome this limitation, remote epitaxy has emerged as a promising technique. In this approach, an atomically thin two-dimensional (2D) interlayer, commonly monolayer graphene is inserted between the substrate and the growing film. The 2D interlayer weakens the chemical bonding between the two crystals while still allowing the substrate's electrostatic potential to influence the overlying growth. As a result, the grown epitaxial film can later be detached as a freestanding nanomembrane and transferred to other platforms, enabling substrate reuse and flexible device fabrication. Despite its enormous potential, achieving true remote epitaxy has been challenging, primarily due to contamination and imperfect interfaces between the graphene and the

substrate. Even trace residues or structural defects on the graphene surface can hinder the transmission of the substrate potential and disrupt epitaxial registry, leading to poor crystal alignment and pinhole formation.

Our research group focuses on addressing these issues by developing an ultra-clean graphene transfer and cleaning workflow for remote epitaxy. We have established a graphene transfer technique that yields atomically clean and defect-free graphene, verified through extensive characterization [18]. This ultra-clean graphene serves as an ideal 2D interlayer for remote epitaxy, minimizing unwanted interactions and promoting uniform crystalline growth. Initially, our group utilized a metal-assisted graphene transfer method integrated with specialized cleaning steps to achieve pristine graphene surfaces suitable for epitaxial growth on robust substrates.

Our current focus is on GaSb substrates as part of an ongoing collaborative project with Dr. Joon Sue Lee's group at the Institute for Advanced Materials and Manufacturing (IAMM) to demonstrate remote epitaxy of Sn and other III–V semiconductors. However, GaSb presents a significant challenge due to its chemical fragility it is easily etched or damaged by the acidic solutions commonly used to remove metal films in metal-assisted graphene transfer. This makes the metal-assisted method unsuitable for GaSb. To address this issue, we have developed a polymer-assisted graphene transfer approach specifically tailored for chemically sensitive substrates like GaSb. This polymer-assisted route enables the safe transfer of graphene without exposing the substrate to corrosive environments.

Furthermore, by integrating our ultra-clean method, which uses atomic Hydrogen cleaning and post-cleaning protocols (explained in the process), we minimize polymer residues and surface contamination that could otherwise introduce defects or pinholes during epitaxial growth. In addition, we are exploring in situ electron beam cleaning (electron source of RHEED can be used) within the molecular beam epitaxy (MBE) chamber to further purify the graphene surface before growth. Together, these combined efforts aim to establish a robust and scalable method for high-quality remote epitaxy across multiple semiconductor systems, overcoming longstanding challenges related to interface contamination, substrate fragility, and lattice mismatch.

6.2 Graphene Growth

Having a graphene layer with a minimum adlayer density is essential for the remote epitaxy [32]. Over the past years, we have understood the factors leading to having a high adlayer density in our monolayer growth process and have been able to grow adlayer-free graphene (Fig. 5.7).

6.3 Cleaning of the Substrate

The presence of contaminants, mainly organic contaminants, must be carefully prevented. If the surface is not thoroughly cleaned, achieving proper adhesion and transfer of the graphene layer onto the substrate becomes challenging, compromising the quality of the remote epitaxy process. Additionally, in molecular beam epitaxial growth, if some residual organics remain on the surface, they cannot be removed unless the samples are heated at rather high temperatures. To ensure a clean surface, the GaSb (001) substrate is sonicated for 10 s sequentially with deionized (DI) water, acetone, isopropyl alcohol (IPA), and then DI water. When transferring from one cleaning agent to another, care

must be taken not to dry the surface, as a dry surface can trap residues, making the surface dirty. Then, the substrate is dried thoroughly using nitrogen (N_2) gas to prevent any residual moisture, which could lead to oxidation or surface contamination. Finally, the substrate is subjected to a UV ozone treatment for 10 minutes to clean the surface further by breaking down and oxidizing any remaining organic contaminants.

6.4 Transferring of Graphene to GaSb Substrate

Graphene is transferred onto the cleaned GaSb substrate using the wet transfer method [39]. The process is briefly summarized in **Figure 6.1**.

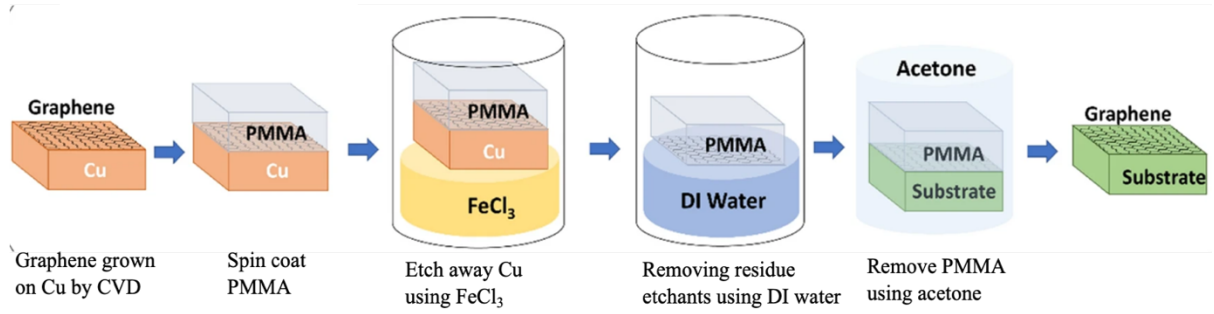


Figure 6.1 Wet transfer method of CVD-grown graphene [39].

6.5 Oxide and Contaminant Removal by Atomic Hydrogen (H)

In literature, the standard practice for remote epitaxy is to use an acid to remove the oxide layer of the semiconductor substrate before the transfer [38,39]. To reduce the amount of organic residue and the oxide between the GaSb substrate and the graphene layer, we adopted an in situ atomic H cleaning. After graphene is transferred onto the GaSb substrate, the sample is inserted into the MBE chamber, and the atomic H is opened for

2.30 hours while increasing the temperature until the growth process starts. There, atomic H penetrates through the graphene and reacts with trapped Oxides and organic contaminants. The volatile products will then move laterally and leave the sample from the uncovered areas of the graphene. In this way, oxygen and volatile organic products can be removed without making pinholes in graphene.

6.6 Epitaxial growth of GaSb

A total of 300 monolayers of GaSb (total thickness 90 nm) are grown on graphene (transferred onto a GaSb substrate). SEM and AFM imaging are done. Still, we could not get the single-crystal film on graphene. But here, the latest images of AFM and SEM are presented (Figure 6.2).

6.7 Future works

Building upon the successful demonstration of clean, single-layer graphene transfer onto GaSb (001) substrates using a polymer-assisted method, future work will focus on optimizing surface preparation and exploring advanced epitaxial growth strategies to fully realize remote epitaxy on chemically sensitive materials.

One of the key directions involves in situ cleaning of the GaSb substrate using atomic hydrogen (H) prior to epitaxial growth. Atomic hydrogen effectively reacts with residual carbon species to form volatile hydrocarbons such as methane, thereby minimizing the accumulation of amorphous carbon on the surface. Moreover, the use of atomic H allows substrate desorption at lower temperatures, reducing potential damage from oxygen evaporation and preserving surface stoichiometry. Implementing this process is expected to further enhance the interfacial cleanliness and the epitaxial coupling between graphene and GaSb, leading to improved remote epitaxy outcomes.

In parallel, integration of in situ electron-beam cleaning within the molecular beam epitaxy (MBE) chamber will be pursued. Utilizing the RHEED electron source for pre-growth surface purification could further eliminate residual contamination on graphene, thereby improving the reproducibility and quality of epitaxial films.

Furthermore, the metal-assisted, polymer-free transfer method developed in this work can be adapted for a variety of chemically robust substrates where direct chemical etching of the metal layer can be performed without damaging the underlying material. This approach provides a clean and scalable route to transfer graphene and other 2D materials while completely avoiding polymer residues, making it an excellent candidate for future applications requiring pristine interfaces and high structural integrity.

Collectively, these developments will advance the scalability and reliability of remote epitaxy-based material synthesis, combining ultra-clean graphene transfer, substrate reusability, and tunable epitaxial control. This integrated approach represents a crucial step toward next-generation semiconductor manufacturing, where reduced material costs and enhanced interface control will play key roles in enabling novel device architectures and quantum technologies.

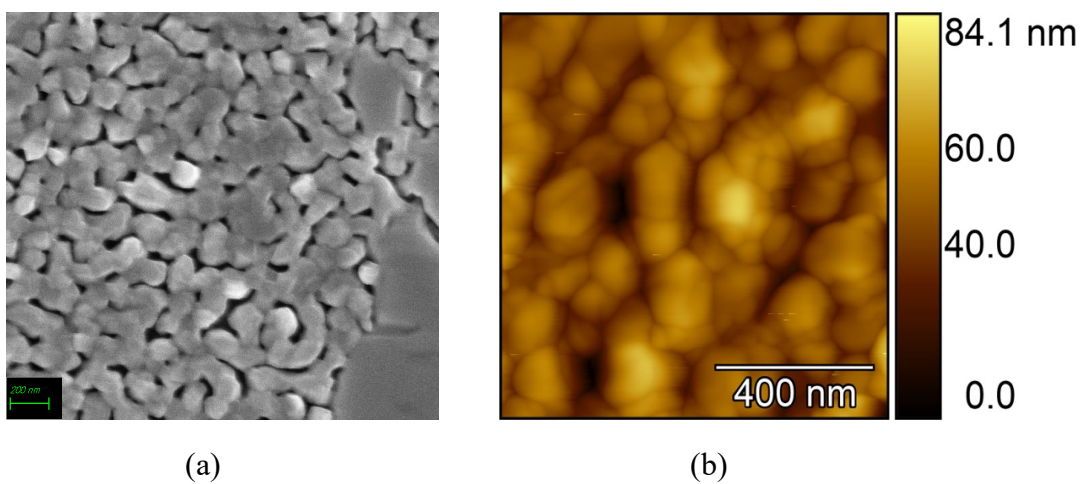


Figure 6.2 (a) SEM (b) AFM images of a 300-monolayer GaSb grown on a GaSb (001)/graphene sample.

LIST OF REFERENCES

- [1] K. S. Novoselov *et al.*, “Two-dimensional gas of massless Dirac fermions in graphene,” *Nature*, vol. 438, no. 7065, pp. 197–200, Nov. 2005, doi: 10.1038/nature04233.
- [2] K. S. Novoselov *et al.*, “Electric Field Effect in Atomically Thin Carbon Films,” Kluwer, 2000. [Online]. Available: www.arXiv.org/quant-ph/
- [3] K. Thakur and B. Kandasubramanian, “Graphene and Graphene Oxide-Based Composites for Removal of Organic Pollutants: A Review,” Mar. 14, 2019, *American Chemical Society*. doi: 10.1021/acs.jced.8b01057.
- [4] Z. H. Khan, A. R. Kermany, A. Öchsner, and F. Iacopi, “Mechanical and Electromechanical Properties of Graphene and their Potential Applications in MEMS.”
- [5] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, “The electronic properties of graphene,” Sep. 2007, doi: 10.1103/RevModPhys.81.109.
- [6] L. P. Biró, P. Nemes-Incze, and P. Lambin, “Graphene: Nanoscale processing and recent applications,” Mar. 21, 2012, *Royal Society of Chemistry*. doi: 10.1039/c1nr11067e.
- [7] M. J. Mohn, J. Biskupek, Z. Lee, H. Rose, and U. Kaiser, “Lattice contrast in the core-loss EFTEM signal of graphene,” *Ultramicroscopy*, vol. 219, Dec. 2020, doi: 10.1016/j.ultramic.2020.113119.
- [8] J. Yuan and L. M. Brown, “Investigation of atomic structures of diamond-like amorphous carbon by electron energy loss spectroscopy.” [Online]. Available: www.elsevier.com/locate/micron

- [9] P. E. Batson, “Carbon 1 *s* near-edge-absorption fine structure in graphite,” *Phys Rev B*, vol. 48, no. 4, pp. 2608–2610, Jul. 1993, doi: 10.1103/PhysRevB.48.2608.
- [10] H. Wang, M. Randeniya, A. Houston, G. Duscher, G. Gu, and M. H. Kao, “Ultraclean Suspended Graphene by Radiolysis of Adsorbed Water Supplementary Information.”
- [11] A. L. Hamon, J. Verbeeck, D. Schryvers, J. Benedikt, and R. M. C. M. V. D. Sanden, “ELNES study of carbon K-edge spectra of plasma deposited carbon films,” *J Mater Chem*, vol. 14, no. 13, pp. 2030–2035, Jul. 2004, doi: 10.1039/b406468m.
- [12] A. Politano, G. Chiarello, and C. Spinella, “Plasmon spectroscopy of graphene and other two-dimensional materials with transmission electron microscopy,” Jul. 01, 2017, *Elsevier Ltd*. doi: 10.1016/j.mssp.2016.05.002.
- [13] M. Saeed, Y. Alshammari, S. A. Majeed, and E. Al-Nasrallah, “Chemical Vapour Deposition of Graphene—Synthesis, Characterisation, and Applications: A Review,” Sep. 01, 2020, *MDPI AG*. doi: 10.3390/molecules25173856.
- [14] A.-S. Johansson, J. Lu, and J.-O. Carlsson, “TEM investigation of CVD graphite on nickel,” 1994.
- [15] G. R. Yazdi, T. Iakimov, and R. Yakimova, “Epitaxial graphene on SiC: A review of growth and characterization,” May 01, 2016, *MDPI AG*. doi: 10.3390/cryst6050053.
- [16] A. Mohsin *et al.*, “Synthesis of millimeter-size hexagon-shaped graphene single crystals on resolidified copper,” *ACS Nano*, vol. 7, no. 10, pp. 8924–8931, Oct. 2013, doi: 10.1021/nn4034019.

- [17] X. Li *et al.*, “Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils,” *Science (1979)*, vol. 324, no. 5932, pp. 1312–1314, Jun. 2009, doi: 10.1126/science.1171245.
- [18] H. Wang, M. Randeniya, A. Houston, G. Duscher, and G. Gu, “Ultraclean Suspended Graphene by Radiolysis of Adsorbed Water,” *Nano Lett*, vol. 24, no. 29, pp. 8866–8871, Jul. 2024, doi: 10.1021/acs.nanolett.4c01440.
- [19] P. Y. Huang *et al.*, “Grains and grain boundaries in single-layer graphene atomic patchwork quilts,” *Nature*, vol. 469, no. 7330, pp. 389–392, Jan. 2011, doi: 10.1038/nature09718.
- [20] W. Regan *et al.*, “A direct transfer of layer-area graphene,” *Appl Phys Lett*, vol. 96, no. 11, Mar. 2010, doi: 10.1063/1.3337091.
- [21] A. W. Robertson and J. H. Warner, “Atomic resolution imaging of graphene by transmission electron microscopy,” *Nanoscale*, vol. 5, no. 10, pp. 4079–4093, May 2013, doi: 10.1039/c3nr00934c.
- [22] M. H. Gass, U. Bangert, A. L. Bleloch, P. Wang, R. R. Nair, and A. K. Geim, “Free-standing graphene at atomic resolution,” *Nat Nanotechnol*, vol. 3, no. 11, pp. 676–681, 2008, doi: 10.1038/nnano.2008.280.
- [23] T. Eberlein *et al.*, “Plasmon spectroscopy of free-standing graphene films,” *Phys Rev B Condens Matter Mater Phys*, vol. 77, no. 23, Jun. 2008, doi: 10.1103/PhysRevB.77.233406.
- [24] J. C. Idrobo and W. Zhou, “A short story of imaging and spectroscopy of two-dimensional materials by scanning transmission electron microscopy,” *Ultramicroscopy*, vol. 180, pp. 156–162, Sep. 2017, doi: 10.1016/j.ultramic.2017.02.002.

- [25] P. E. Batson, “Carbon 1s near-edge-absorption fine structure in graphite.”
- [26] D. V Badm, “X-RAY STUDIES OF GRAPHITE FORMED BY DECOMPOSING SILICON CARBIDE,” Pergamon Press Ltd, 1965.
- [27] R. Yakimova *et al.*, “Analysis of the formation conditions for large area epitaxial graphene on SiC substrates,” in *Materials Science Forum*, Trans Tech Publications Ltd, 2010, pp. 565–568. doi: 10.4028/www.scientific.net/MSF.645-648.565.
- [28] K. V. Emtsev *et al.*, “Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide,” *Nat Mater*, vol. 8, no. 3, pp. 203–207, 2009, doi: 10.1038/nmat2382.
- [29] W. Norimatsu and M. Kusunoki, “Epitaxial graphene on SiC{0001}: Advances and perspectives,” Feb. 28, 2014. doi: 10.1039/c3cp54523g.
- [30] Robin F.C. Farrow, *Molecular Beam Epitaxy, applications to key materials*. NOYES, 1995. Accessed: Oct. 07, 2024. [Online]. Available: https://books.google.com/books?hl=en&lr=&id=wToPhW5TZosC&oi=fnd&pg=PP1&dq=epitaxial+applications&ots=ISBzdn0n--&sig=pYSE_ahiHfCLCYnk9EyQhBu-p54#v=onepage&q&f=false
- [31] I. Roh *et al.*, “Applications of remote epitaxy and van der Waals epitaxy,” Dec. 01, 2023, *Korea Nano Technology Research Society*. doi: 10.1186/s40580-023-00369-3.
- [32] X. Han *et al.*, “Remote Epitaxy and Exfoliation of GaN via Graphene,” *ACS Appl Electron Mater*, vol. 4, no. 11, pp. 5326–5332, Nov. 2022, doi: 10.1021/acsaelm.2c00997.
- [33] C. S. Chang *et al.*, “Remote epitaxial interaction through graphene,” 2023. [Online]. Available: <https://www.science.org>

- [34] Y. Kim *et al.*, “Remote epitaxy through graphene enables two-dimensional material-based layer transfer,” *Nature*, vol. 544, no. 7650, pp. 340–343, Apr. 2017, doi: 10.1038/nature22053.
- [35] H. Wang, M. Randeniya, A. Houston, G. Duscher, and G. Gu, “Ultraclean Suspended Graphene by Radiolysis of Adsorbed Water,” *Nano Lett*, vol. 24, no. 29, pp. 8866–8871, Jul. 2024, doi: 10.1021/acs.nanolett.4c01440.
- [36] S. F. Mousavi *et al.*, “Atomic Hydrogen Annealing of Graphene on InAs Surfaces and Nanowires: Interface and Morphology Control for Optoelectronics and Quantum Technologies,” *ACS Appl Nano Mater*, vol. 5, no. 12, pp. 17919–17927, Dec. 2022, doi: 10.1021/acsanm.2c03891.
- [37] P. Neta, “REACTIONS OF HYDROGEN ATOMS IN AQUEOUS SOLUTIONS.” [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [38] H. Wang, M. Randeniya, A. Houston, G. Duscher, G. Gu, and M. H. Kao, “Ultraclean Suspended Graphene by Radiolysis of Adsorbed Water Supplementary Information.”
- [39] J. Ji *et al.*, “Understanding the 2D-material and substrate interaction during epitaxial growth towards successful remote epitaxy: a review,” Dec. 01, 2023, *Korea Nano Technology Research Society*. doi: 10.1186/s40580-023-00368-4.

APPENDIX

VITA

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