Synthesis of Bilayer Graphene and Hexagonal Boron Nitride by Chemical Vapor Deposition Method

By

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Abstract

The aim of this thesis is two-fold: the first is to develop a reliable method for synthesizing bilayer graphene using chemical vapor deposition (CVD) method and to understand the growth mechanism. The second part involves exploring methods of synthesizing hexagonal boron nitride (hBN). The successful isolation of monolayer graphene in 2004 has attracted many researchers to search for potential applications of graphene and other two-dimensional materials in electronic and optical devices. However, the Scotch-tape method sets contraints for such applications due to the limited size and randomized location of obtained flakes. Thus, synthesizing large-area, high-quality two dimensional materials is highly desirable. This thesis seeks to develop a method to produce both bilayers and hBN with large area by CVD method and to investigate the underlying growth mechanisms for better control over the thickness, uniformity and stacking orientation.

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Title: Professor
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Chapter 1: Introduction

Since the first successful isolation of graphene using Scotch-tape methods, many layered materials were explored, such as hexagonal boron nitride (hBN), transition metal dichalcogenides (TMD) and black phosphorus (BP). Layered materials have atoms strongly bonded within the plane while weakly bonded between layers by van der Waal's force, which allows these materials to be cleaved. In this thesis, these isolated layered materials with one to a few number of layers are referred as two-dimensional (2D) materials.

In contrast to conventional bulk materials such as silicon (Si), gallium nitride (GaN) and gallium arsenide (GaAs), these 2D materials show many exotic properties due to the quantum confinement in the direction vertical to the plane. More importantly, 2D materials are considered to cover the a wide range of band structures necessary for building electronic devices, including graphene as a semimetal for interconnects (Figure 1.1(a)), hBN as the insulating dielectric barrier (Figure 1.1(b)), and semiconducting TMD materials (Figure 1.1(c)) or recently-discovered narrow band gap black phosphorus (Figure 1.1(d)) as the active channels. In particular, graphene has a zero band gap and can serve as contacts to other 2D materials, with the capability of sustaining current densities of more than $10^9 \text{ A/cm}^2$. Additionally, the work function of graphene can be controllably tuned by electrostatical doping or chemical doping, in order to adapt to different work functions of other 2D materials. Moreover, hBN was reported as an excellent dielectric materials with a dielectric constant of $\sim 3-4$, and a breakdown fields of $\sim$
8V/nm, which is similar to SiO2 thin film. TMD materials such as MoS2 and WSe2 have been used to show exceptional switching current ratio up to $10^8$.15-17

Figure 1.1 The atomic structures and the corresponding band structures of (a) graphene, (b) hBN, (c) MoS2 and (d) black phosphorus.1
Furthermore, 2D materials have advantages over 3D materials when it comes to device architecture. First, the absence of dangling bonds at the interface can overcome problems such as surface traps and interfacial states, which are responsible for device degradation.\textsuperscript{18} Furthermore, heterostructures using 2D materials are stacked with van der Waal’s force; therefore, there are no constraints in lay stacking from lattice mismatch. Many devices based on heterostructures of 2D materials have been reported. For instance, Britnell et al. reported tunneling transistors based on graphene as tunneling electrodes and hBN and MoS\textsubscript{2} as the barrier. The devices exhibited room-temperature switching ratios of $\sim$50 and $\sim$10000, respectively.\textsuperscript{15} Bertolazzi et al. demonstrated a nonvolatile memory cells using a MoS\textsubscript{2} and graphene heterostructure.\textsuperscript{19} Recently, both Lee et al. and Roy et al. demonstrated field-effect transistors using heterogeneously stacked two-dimensional materials for all components, where graphene films were used as the source, drain and the top-gate contacts, hBN as the top-gate dielectric layer, and MoS\textsubscript{2} as the active channel material as shown in Figure 1.2.\textsuperscript{20,21} In their papers, the transistors exhibit n-type behaviors with an ON/OFF current ratio of $\sim$106 and an electron mobility of more than 30 cm\textsuperscript{2} /Vs. Moreover, the mobilities of their devices did not degrade at high gate voltages, which shows advantages over conventional Si transistors where enhanced surface roughness scattering severely reduces carrier mobilities at high gate-fields. In addition, Lee et al. demonstrated flexible and transparent devices on a polymer substrates that show unchanged performance up to 1.5\% strain, resulting from the superior mechanical strength and flexibility of these 2D materials.\textsuperscript{21} These results show the benefits of using layered material systems for future electronic devices, in particular, when devices requires flexibility and transparency.
1.1 Structure and Properties of Bilayer Graphene

Bilayer graphene is composed of two layers of monolayer graphene. Graphene has shown a wealth of exceptional properties such as high carrier mobility, high thermal conductivity, high Young’s modulus, and optical transmittance defined by fundamental constants. However, monolayer graphene has a linear gapless band structure. The lack of an energy gap in its electronic structure leads to its low on-off ratio in graphene transistors (typically <10 at room temperature). With most electronic applications relying on the presence of a band gap, the recent observation of the band gap opening induced in AB-stacked bilayer graphene makes it attractive for applications such as pseudospintronics, terahertz technology, and infrared nanophotonics. For AB-stacked bilayer graphene, the carbon atoms of the top layer (grey) sit over the center of the hexagon of the six-carbon ring of the bottom layer (black), as shown in Figure 1.3 (b). The band diagram of AB-stacked bilayers stacked in the Bernal AB stacking order shows that the lowest conduction band touches the highest valence band with a zero band gap (Figure. 1.3 (e)). However, when a vertical electrical
field is applied across the two layers (Figure. 1.3 (d)), a nonzero bandgap can be induced by symmetry breaking, and the bandgap is tunable depending on the electric field. For turbostratic bilayer graphene, the top layer is rotated with respect to the bottom layer and the electronic structures are dependent on the rotational angles (Figure. 1.3 (c)). At large angles (>20°), the layers become completely decoupled and the electronic properties resemble those of a single-layer graphene. As rotational angles become smaller, there is a decrease in the carrier velocity which is strongly angle dependent. At the smallest angles, exotic electrical properties are observed, such as the localization of Dirac electrons and van Hove singularities. Because bilayers with larger rotational angles behave as two isolated monolayers, the electrical conductivity is improved, making them an excellent candidate for next generation transparent electrodes.

Figure 1.3 Top view of the arrangement of carbon atoms in (a) monolayer graphene, (b) an AB-stacked bilayer and (c) turbostratic bilayers. (d), Illustration of a cross-sectional side view of a top- and bottom-gated bilayer graphene device. The sketch shows how gating of the bilayer induces top (Dₜ) and bottom (Dₜ) electrical displacement fields. (e) Left, the electronic structure of a pristine bilayer has a zero bandgap. Right, upon gating, the displacement fields induce a non-zero bandgap.
The applications of bilayer graphene are discussed, depending on the stacking orientations and the resulting electronic structures. For AB-stacked bilayer, because of its tunable transport\textsuperscript{48-50} and optical properties\textsuperscript{51}, it shows advantages over monolayer graphene in applications, such as field-effect transistors (FETs), pseudospintronics and other electronic applications. For instance, it is difficult to apply monolayer graphene to transistor devices due to the lack of band gap. In contrast, dual-gated bilayer graphene FETs with on/off ratio as high as 100 at room temperature hold promise for flexible and gate-tunable light emitting devices and light detectors. Szafranek et al. demonstrated that bilayer-graphene based FETs exhibit a voltage gain of 35, a factor of six higher than they could attain in monolayer graphene-based FETs.\textsuperscript{52} Moreover, graphene-based pseudospintronics exploits another advantage of bilayer graphene; in contrast to monolayer graphene, when a band gap is induced in bilayer graphene, the pseudospin direction can be switched by inverting the sign of the applied potential difference.\textsuperscript{53} This effect can be utilized to realize a pseudospin-based analogue of a spin valve with a large on-off ratio. Additionally, Yan et al. had demonstrated a hot-electron bolometer based on bilayer graphene that outperforms commercial silicon bolometers with several times lower noise-equivalent power and three to five orders of magnitude higher intrinsic speed.\textsuperscript{54} On the other hand, a turbostratic bilayer with a reduced sheet resistance can serve as electrodes for solar cells.\textsuperscript{20-23} A single layer of graphene does not have sufficiently high sheet conductivity for such applications so stacking multilayers together and/or doping graphene layers is needed.\textsuperscript{20} Li et al. has shown that the sheet resistance decreases from 1000 $\Omega$/sq to 500 $\Omega$/sq when they use turbostratic bilayer graphene instead of monolayer.\textsuperscript{21} However, the transfer process is tedious and it usually causes tears or holes, resulting in device failure. Therefore, direct synthesis of bilayers can help improve the overall graphene film reliability by reducing the number of transfers. In summary, the realization of bilayer graphene-based devices in photonics and optoelectronics requires large-area high-quality AB-stacked bilayer graphene samples. In
most experiments, AB-stacked bilayer graphene was obtained from mechanical exfoliation, which sets constraints on size and location. On the other hand, for large-area turbostratic bilayers, the layer-by-layer transfer processes is time-consuming. Therefore, it is highly advantageous for the aforementioned applications to synthesize large-area high quality bilayers with stacking control.

1.2 Structure and Properties of Hexagonal Boron Nitride

Hexagonal boron nitride is composed of alternating boron and nitrogen atoms arranged in a similar structure to graphene, however, with ionic bonds in a plane and a weak van der Waals force between the layers. In contrast to graphene, hBN has AA' stacking with B atoms placed directly above the N atoms, as shown in Figure 1.4.\textsuperscript{55} hBN powder was traditionally used as a lubricant additive.\textsuperscript{56} Since hBN is chemically inert to a wide variety of acids and oxidizers even at high temperature,\textsuperscript{57,58} it has been used for coating materials.\textsuperscript{59} In addition to its chemical innerness and thermal stability, hBN has a large direct band gap of ~ 5.78eV, making it a good insulator.\textsuperscript{60} Utilizing the large band gap of hBN, Kubota \textit{et al.} demonstrated hBN-based deep ultraviolet emitters\textsuperscript{60} and Watanabe \textit{et al.} demonstrated hBN-based far-ultraviolet (FUV) light-emitting diodes (LEDs). More recently, hBN has shown great promise to be used for dielectric layers and tunneling barriers.\textsuperscript{61-63} For instance, Britnell \textit{et al.} have demonstrated that the tunneling current in a tunnel diode using hBN film as a barrier layer decreases exponentially with the decreasing number of hBN layers.\textsuperscript{62}
Furthermore, the hBN films have served as an effective substrate for graphene or other 2D materials due to the sub-atomic smoothness and the absence of dangling bonds. Many studies have shown that using hBN as the substrate can enhance the mobility in graphene by an order of magnitude. In addition, hBN can improve the performance of graphene devices at high temperature and under a high electric field, resulting from less scattering by interfacial phonons on hBN, as compared to that on a SiO₂ substrate. Moreover, hBN has a lattice constant similar to that of graphene. It was suggested that due to the close match of the lattice parameters between hBN and graphene, when the lattices of graphene and hBN are aligned, a band gap could be induced in graphene.

Many papers have reported the synthesis of large-area hBN by CVD using Ni and Cu foils. However, there is little control over the uniformity and the number of layers for hBN grown using Ni. For hBN grown on Cu, Kidambi et al. showed that B atoms are dissolved into the bulk of Cu but the amount of N dissolved in Cu is negligible. Thus, the quality of hBN grown on Cu is compromised. Therefore, improvement of the crystallinity of large area hBN films is still required for electronic applications. Recently, extensive work has been done to prepare high-quality monolayer hBN using Pt foil as the
substrate.72-74 Moreover, our group has also developed the synthesis of multilayer hBN using Fe foil. This thesis will focus on using the CVD method to synthesize monolayer to few layer hBN using Pt and Fe foils.

1.3 Thesis Organization

This thesis discusses the scalable synthesis of large-area bilayer graphene and hBN by the CVD method, and to study the underlying growth mechanism for improving the quality of the resulting graphene and hBN films.

Chapter 2 reviews the synthesis methods of bilayer graphene and hBN. In particular, the CVD methods for preparing bilayer graphene and hBN are discussed in detail. The growth mechanism of each method is presented, and the advantages and limitations are summarized.

Chapter 3 summarizes the experimental details and gives an overview of the synthesis and characterization procedures for both bilayer graphene and hBN since the procedures share some similarities. The procedures are divided into four parts: preparation of materials, growth processes, transfer techniques and characterization methods. The important aspects of each process are described in detail.

Chapter 4 investigates the synthesis and characterization of bilayer graphene on Cu enclosures by CVD. Using isotope labeling, a rapid method has been developed for identifying the stacking orientation and the growth sequence of bilayers. The growth mechanism of the bilayer graphene is analyzed by studying the growth behavior on both sides of the Cu enclosure. A growth model is presented and the model is further confirmed by Cu thickness dependence studies. Finally, the diffusion mechanism has been applied for the growth of large-area single-crystal monolayer graphene free of bi-/tri-layers.
Chapter 5 describes the synthesis and characterization of the hBN growth. Two substrates – Fe and Pt – were used in the experiment and the resulting hBN films is discussed. The studies revealed that thick hBN can be prepared on Fe, following a precipitation mechanism. Moreover, monolayer hBN growth on Pt is demonstrated.

Finally, the conclusions of this thesis and suggestions for future research are presented in Chapter 6.
Chapter 2: Synthesis of Bilayer Graphene and Hexagonal Boron Nitride

In this chapter, the synthesis method of both bilayer graphene and hBN will be discussed. For bilayer graphene, we summarize all types of fabrication methods; however, we will primarily focus on chemical vapor deposition methods, which has been widely reported as a scalable method for successfully preparing large-area and high-quality bilayer. The mechanism for each method will be discussed in detail as well as advantages and limitations. For hBN, it does not occur in nature and it is still challenging to develop a reliable and robust synthesis method; therefore, we will review the history of the synthesis of hBN and discuss the CVD method in particular.

2.1 Fabrications of Bilayer Graphene

Extensive research has been carried out on the scalable synthesis of bilayer graphene. This is because the size of bilayer graphene flakes prepared by the Scotch-tape method is limited and with very little control over the thickness or shape of the flakes.75,76 Layer-controlled chemical exfoliation processes were reported to produce large-quantity bilayers.77 Nevertheless, the quality of the bilayers by chemical exfoliation (≈1kΩ resistivity and ≈400 cm²V⁻¹s⁻¹ hole mobility) is not comparable to that prepared by mechanical exfoliation due to defects introduced during the exfoliation processes. Synthesis of large-area (200 × 200 μm²) epitaxial AB-stacked bilayer graphene was
demonstrated on atomically flat 4H-SiC (0001) step-free mesas, but this substrate is extremely expensive. Recently, many papers have reported using CVD methods for producing bilayer graphene.

The CVD method has advantages of being inexpensive and can produce large-area high-quality bilayers that can be readily transferred to other substrates for characterization and device fabrication. For example, several groups have reported methods of synthesizing bilayer graphene via CVD by controlling the carbon solubility of the catalyst, for example, using Cu-Ni alloy foils or Cu-Ni thin films. However, bilayer graphene grown by increasing the carbon solubility of the substrate relies on a careful control of the alloy composition and the precipitation rate. Another approach to growing bilayers on copper involves introducing external carbon sources to deposit an additional layer on top of an existing monolayer. In addition, direct growth of large-domains of bilayer graphene from underneath discontinuous monolayer domains has also been reported, but with relatively low bilayer coverage.

There are two general routes for graphene growth on metal by CVD: via precipitation or via a surface-mediated reaction (Figure 2.1). The properties of the metal substrate used during the growth determines which graphene growth mechanism dominates. For precipitation, there are two important differentiating characteristics: the substrate exhibits high carbon solubility and/or a tendency for a metastable carbide formation which later decomposes into metal and carbon. Using Ru as an example of a metastable substrate, Ru has moderate carbon solubility but does not form any carbide. One to two layers of graphene can form on Ru by precipitation of interstitial carbon from the bulk of Ru. Meanwhile, for some other metals, the graphitization process could be a mixture of the two, so one needs to consider both the temperature-dependent solubility of carbon and the stability of the carbide formation. The stability of the carbide formation varies greatly so we need to consider two scenarios. First, consider the case where the carbide formation is not stable. For instance, it is shown that the formation
of the metastable Ni$_2$C phase promotes the precipitation of carbon from Ni to form graphene.\textsuperscript{41, 89-94} Next, if the metal carbide is very stable, it is hard for carbon to be released from the carbide to form graphene/graphite. As an example, recently IVB-VIB metals (Ti, Zr, Hf, V, Nb, Ta, Mo, and W) were reported as substrates to grow monolayer graphene.\textsuperscript{95} When carbon atoms dissolve into these metals, stable carbides form in the bulk. The carbide formation is so stable that it prevents carbon from being released; consequently, it fully suppresses carbon precipitation on the surface, leading to monolayer graphene by surface catalytic growth.

The other mechanism of preparing graphene is by a surface-mediated reaction. The characteristics of the metals for this mechanism are: low affinity to carbon and/or with low carbon solubility. Typical examples are Cu\textsuperscript{96} and Au\textsuperscript{97}. For example, Cu has low carbon affinity due to a filled 3d-electron shell. Thus, it does not form any carbide phases\textsuperscript{98, 99} and has very low carbon solubility compared to other metals, such as Ni or Co\textsuperscript{100-102}. It is commonly understood that graphene grows on Cu in the following way: hydrocarbons get catalytically decomposed on the Cu surface first. Then, the graphene nucleates and grows till the entire exposed Cu surface gets fully covered. Since the carbon solubility is low in Cu, a minimal concentration of carbon atoms can diffuse into the bulk.

In short summary, for precipitation, the formation of graphene films is more complicated: we need to consider the amount of carbon dissolved (carbon solubility) and segregated (stability of carbide formation and the cooling conditions). As a result, the amount of carbon precipitated out is highly dependent on the conditions and it becomes challenging to control the number of layers and the thickness uniformity on the surface. In contrast, although surface-mediated reactions usually only give a monolayer of graphene, the process is simpler because only one mechanism is involved. Therefore the discussion of this review will put more emphasis on the surface mediated growth. Among these metals that have low carbon solubility and low carbon affinity, we will mainly
focus on Cu due to low cost, etchability, and compatibility with the semiconductor industry.

Recently, many papers reported on the synthesis of large-area high-quality bilayer graphene. Based on the strategies of growing bilayer graphene, we divide our discussions into the following categories: (1) using the precipitation method, (2) using a surface mediated-reaction, (3) others.

(a) Precipitation
(b) Surface-mediated Reaction

Figure 2.1 Schematic diagrams of the growth mechanism of graphene via (a) precipitation and (b) a surface-mediated reaction.¹⁰³

2.1.1 Using Precipitation Method

Following the earlier discussion, precipitation allows the preparation of multilayer graphene films. However, to achieve a more uniform bilayer graphene, using this mechanism needs careful control of the amount of carbon (i) dissolved into and (ii) precipitated out of the substrate or a combination of both. For example, Reina et al. reported bilayer graphene growth with improved uniformity on a Ni thin film with a controlled carbon precipitation process.⁹⁰,⁹¹ Under a diluted CH₄ concentration (0.5%), they employed a slow cooling rate (~4°C/min) to decrease the number of nucleation sites of multilayer graphene (Figure 2.2 (a)). Another method to control the amount of carbon source is to predetermine a fixed amount of carbon sources (Figure 2.2 (b)). Yan et al. deposited solid carbon sources of different thickness to control the number of graphene
layers.\textsuperscript{104} It is worth noting that several papers have reported bilayer graphene growth using a Cu-Ni alloy.\textsuperscript{105-107} For instance, Liu \textit{et al.} used a metal thin film composed of Cu and Ni layers (Figure 2.2 (c))\textsuperscript{105, 107} and Wu \textit{et al.} used commercial Cu-Ni alloy foils (weight percent: 88.00\% Cu, 9.90\% Ni) (Figure 2.2 (d)).\textsuperscript{81} Since Cu and Ni are well-known binary systems\textsuperscript{108}, Cu and Ni combined is anticipated to be a suitable system for controllable carbon solubility by tuning the atomic fraction of Ni in Cu. (Ni has high carbon solubility about 1.3 atom \% of carbon in Ni while Cu has less than 0.001 atom \% of carbon in Cu at 1000\textdegree C.\textsuperscript{109, 110})

In the above mentioned methods, the carbon dissolution-precipitation process is controlled by slowing down the cooling rate, fixing the amount of the carbon dissolved, and tuning the carbon solubility in the metal substrates. The advantage of this method is that the coverage of bilayers is high (>70\%). However, several drawbacks need to be taken into consideration. First, the thickness of the graphene is not uniform, as shown in Figure 2.2 (a) and 2.2 (e). For Ni thin films, it is shown that multilayers prefers to precipitation at the grain boundaries.\textsuperscript{111} For Ni-Cu alloys, multilayers can also be observed during the growth process. Second, the domains are relatively small (~10\textmu m or less). These small domains are due to the difficulty in controlling the nucleation density during the precipitate process. Furthermore, as for the stacking orientation, the bilayer grown using pure Ni is random, consistent with previous reports.\textsuperscript{111} Interestingly, in contrast, the analysis using Raman mapping in these papers has shown that bilayers grown on Cu-Ni alloy by precipitation are mostly AB-stacked (98\%).\textsuperscript{49, 65, 66} The reason for AB-stacking is not fully explained but the results would be more convincing if a larger-area analysis could be performed.
Figure 2.2 Synthesis of bilayer graphene using precipitation methods. (a) Effect of the cooling rate on Ni films using a CH₄ concentration of 0.5%. 90 (b) Growth procedures of bilayer graphene derived from polymers or SAMs on SiO₂/Si substrates by annealing the sample in an H₂/Ar atmosphere at 1000°C for 15 min. 91 (c) Schematic illustration of sandwiched Cu/Ni/SiO₂/Si segregation structure and optical microscope images of bilayer graphene segregated from Cu-Ni alloy by regulating the Ni content in the alloy. 92 (d) Schematic diagrams of the growth process of carbon isotope labeled graphene, and
the possible distribution of $^{12}$C and $^{13}$C atoms in graphene films and inside the Cu-Ni alloy. The gray and blue balls represent the $^{12}$C and $^{13}$C atoms, respectively.\(^{81}\) (e) Optimization of 2–3 layer graphene growth on Cu–Ni (1200/400 nm) film. Before flowing methane, Cu–Ni film was annealed at 990 °C and 20 mbar and in 100 sccm H\(_2\)/150 sccm Ar for 30 min. The growth temperature is 920 °C. (A) 0.5 mbar, 5 sccm H\(_2\), 8 sccm CH\(_4\), for 120 s. (B, C, and D) 0.1 mbar, 5 sccm H\(_2\), for 120 s with 3 sccm CH\(_4\), 6 sccm CH\(_4\), and 8 sccm CH\(_4\), respectively. (E, F) 0.2 mbar, 5 sccm H\(_2\), for 120 s with 8 sccm CH\(_4\) and 10 sccm CH\(_4\), respectively. Scale bar is 30 μm.\(^{106}\)

### 2.1.2 Using the Surface Mediated-reaction Method

Under low pressure CVD conditions, the graphene growth on Cu is self-limited and the growth terminates when the Cu is fully covered by monolayer graphene. Therefore, the general strategy to grow two layers of graphene by surface mediated-reaction is to increase/prolong the time of active catalytic area or to provide additional catalytic surfaces. It is reported that by using a high H\(_2\) ratio, and/or a very low CH\(_4\), the growth rate of the monolayer will be slowed down, therefore keeping the Cu surface uncovered and giving the second layer more time to grow. Another approach is to place an additional Cu surface upstream to provide a carbon source for the second layer to form in the downstream. Furthermore, the inside surface of the Cu enclosure also acts as an extra surface under a different growth condition that furthermore provides a carbon source for bilayer growth on the outside surface of the Cu enclosure.

#### 2.1.2.1 Using High H\(_2\) and/or Low CH\(_4\) Concentration to Prolong the Exposed Cu Area

Large-domain bilayers can be achieved with the second layer growing underneath by using a very low CH\(_4\)/H\(_2\) ratio. Many papers have reported large-domain bilayer flakes on the inside of the Cu enclosures.\(^{80, 112}\) Li \textit{et al.} proved that on the inside of the enclosure, the second layer grows from underneath the first layer. The growth mechanism was proposed as follows: inside the Cu enclosure, the CH\(_4\) concentration is extremely
low. Therefore, the growth rate is very slow, leading to more exposed Cu. At the same time, since the growth of the monolayer is slow, it allows more time for the bilayer to grow by diffusing at the interface between Cu and the monolayer graphene. A similar approach was reported by Zhou et al. to grow large-domain AB-stacked bilayer graphene flakes. They prepared graphene on a flat Cu substrate instead of a Cu enclosure; therefore, to achieve a very low CH$_4$ concentration, they used a H$_2$/CH$_4$ ratio of 4400. It should be noted that Nie et al. has also shown that on the flat Cu foil, the second layer grows from underneath by using the LEEM/LEED technique. Thus, we believe that growth mechanism is similar to the former case.

The aforementioned direct synthesis methods produce large single-domain high-quality bilayers. Moreover, in these experiments, most of the bilayers are found to be AB-stacked, suggesting some kind of "template" mechanism from the top graphene layer. Nevertheless, these methods have several limitations. First, the bilayers grow as discrete flakes instead of as a continuous film. Once the monolayer graphene coalesces together, the growth of the bilayer ceases because there is no available catalytic Cu or open channel for the diffusion process. Second, usually multilayers (three or more than three layers) grow hand-in-hand with the bilayers. Lastly, the growth rate is so slow that the growth process takes a long time (>2 hours). To obtain a large second layer, which grows underneath the monolayer flakes, a high H$_2$ to CH$_4$ ratio is used to slow down the growth rate of the monolayer, but this slows down the growth of the second layer as well. Additionally, when active carbon species are formed on the catalytic Cu surface, it was suggested by calculations that most of the carbon at once would be captured by the edges of the first layer and contribute to the monolayer growth, and only a small percentage of the carbon atoms would diffuse underneath the monolayer. Also, as the monolayer grows larger, the distance for the carbon atoms to flow in order to diffuse to the edges of the buried second layer increases, resulting in a decreasing growth rate of the bilayer as time proceeds.
2.1.2.2 Providing Additional Catalytic Surface using Flat Cu

The second method of growing bilayer by a surface-mediated reaction is to introduce an additional catalytic surface. Usually a fresh Cu foil is used to generate carbon radicals or fragments in the upstream. Then the free carbon sources can transport over a certain distance in the reactor and deposit on the existing graphene/Cu downstream. The second layer forms on top of the existing graphene, and thus is not in contact with the catalyst. Nevertheless, the boundaries and impurities on the existing target graphene/Cu could serve as nucleation sites for the epitaxial growth of the additional layer.

Yan et al. reported AB-stacked bilayer graphene growth with a coverage of up to 67% and single bilayer domain sizes as large as 50 μm using this method. They used a two-zone furnace with each piece of Cu placed in both heating zones. Once the growth of the monolayer was completed in the second zone, so that the first zone is activated and the Cu foil upstream can catalyze more carbon sources (Figure 2.3 (a)). Another method was reported with bilayer coverage up to 99% using a 6 cm Cu foil stripe (Figure 2.3(b)). In the paper, the authors employed a high H₂/CH₄ ratio (40:1) so that the Cu surface at the upstream end remains partially exposed and thus catalytically active throughout the whole growth process.

These bilayer synthesis methods used additional exposed Cu regions upstream to catalyze CH₄ to generate carbon sources for the formation of the second layer on the existing graphene downstream. This method allows for high-coverage (>70%) and high-quality bilayers. Additionally, it was proposed that in this way, the second layer form on the existing graphene as the template, and the resulting bilayers should then be AB-stacked. The downsides of this method are that the distance between the fresh Cu surface and the graphene/Cu samples is critical and the results depend very sensitively upon this distance. Only a small region of the Cu downstream is in the sweet spot regions for
bilayer formation. The remaining regions have no bilayers, or the coverage is much lower. For example, in the experiment using a two-zone furnace, the large coverage bilayers only form in the center of the Cu downstream. While in experiment with long Cu stripes, variance in coverage can be observed, depending on the distance from the upstream. High coverage bilayers can only be achieved at the location which is about 5 mm away from the upstream edge. Furthermore, the nucleation sites are random, usually depending on the surface morphologies of the graphene such as wrinkles, boundaries, and defects of the underlying graphene. The size and shape of the bilayer flakes would deform into hexagons or round disks. It is interesting that these growth methods seem to produce exclusively bilayers instead of tri- or multi-layers. If carbon atoms/fragments can be simply deposited onto the surface of an existing graphene film, we would expect a layer-by-layer epitaxial method to produce a graphene film with a precise number of layers. However, in either of the papers, no more than two layers were reported. This suggests the possibility of some remaining catalytic effects of the Cu substrates underneath the monolayer graphene without direct contact to the second grown layer. It is possible that the third layer cannot be formed because the catalytic effect of the underlying Cu is diminished or screened by the two layers of graphene. However, follow-up on this issue will require further systematic studies.
Figure 2.3 Synthesis of bilayer graphene through a surface-mediated reaction which introduces an additional catalytic surface. (a) A schematic drawing of the bilayer graphene growth mechanism involving gas-phase carbon radicals and aromatic fragments transported and epitaxially grown on a monolayer graphene surface. SEM images of CVD grown bilayer graphene. (b) Carbon fragments coming from the uncovered upstream Cu catalyst are continuously transported downstream for the growth of bilayer graphene. SEM images of monolayer (1L) and bilayer (2L) graphene at the upstream end and center of the Cu substrate, respectively. The bright strips are the exposed copper surface between graphene domains, and the darker hexagonal contrast corresponds to the bilayer graphene. Scale bars are 20 μm. (c) The upper picture is the photographic image of a Cu foil strip (1.5 × 6.0 cm) with bilayer graphene. The lower pictures are a series of optical images of graphene along the different positions of the Cu foil starting from the upstream end.

2.1.2.3 Other Methods

There are many other reports on the synthesis of bilayers. Although some of the growth mechanisms are not clearly discussed or proven convincingly, we would like to include our understanding of the growth mechanisms here. The general trend is: if there is a relatively high partial pressure of carbon species, the carbon radicals will
graphitize on the Cu surface to form a thicker graphene layer. Moreover, the thicknesses of the graphene layers are dependent on the partial pressure of the carbon sources; a higher carbon partial pressure favors the growth of thicker graphene films. For example, Bhaviripudi et al. reported that thicker graphene can be observed at various locations and thicker graphene region are observed by increasing the CH$_4$ content at atmospheric pressure CVD (APCVD) (Figure 2.4 (a)).$^{123}$ Similarly, under low pressure CVD (LPCVD), Sun et al. demonstrated that thickness of graphene layer increases when the total pressure increases, while maintaining the same gas composition (Figure 2.4 (b)).$^{124}$ Additionally, similar trends apply to liquid and solid precursors. Many papers have reported bilayer growth using liquid precursors, such as ethane (C$_2$H$_6$), ethanol (C$_2$H$_6$O) and propane (C$_3$H$_8$) (Figure 2.4 (c)).$^{119-122}$ Moreover, to prepare bilayer graphene, solid carbon sources are also used, such as poly(methyl methacrylate) (PMMA), poly(2-phenylpropyl)methysiloxane (PPMS), polystyrene (PS) and poly(acrylonitrile-co-butadiene-co-styrene) (ABS).$^{104,125}$ The decomposition of liquid/solid precursors requires a lower energy pathway than that of CH$_4$.$^{126-129}$ Also, liquid/solid precursors have higher carbon density. Thus, it is anticipated that under similar growth conditions, it is easier to achieve bilayers using liquid/solid precursors. However, using these methods, the grains sizes are relatively small (<5 μm) and there is little control over the location of the bilayer/multilayers.
Figure 2.4 Synthesis of bilayer graphene by using relatively a high partial pressure for the sources of the carbon species. (a) Optical images of the transferred graphene on 300 nm thick SiO₂ substrate synthesized under APCVD conditions using Cu as a catalyst using different CH₄ partial pressures, as indicated. Scale bars: top 20 μm; bottom 10 μm. 123 (b)
SEM images of ethanol-derived graphene using flow rates of 10, 30, 50, and 100 sccm and growth periods of 60 min (top) and 90 min (bottom). The partial pressures of ethanol for these flow rates are approximately 10, 30, 50, and 100 Pa, respectively. (c) SEM images of graphene grown with ethane at increasing pressures show the appearance and growth of a second layer. Coverage statistics were tabulated and graphed below to illustrate the growth trends of graphene layers at different pressures. Scale bar is 1 μm.

2.2 Fabrications of Hexagonal Boron Nitride

While highly ordered pyrolytic graphite (HOPG) graphene is widely accessible, it is not the same for hBN. This is because hBN does not exist in nature and it is challenging to synthesize. There are mainly three representative methods of synthesizing hBN thin film or bulk; the precipitation method, the CVD method, and ultra-high-vacuum (UHV) deposition method.

The precipitation method leads to high quality crystalline boron nitride. Currently, the hBN samples used in most of the experiments were prepared by the Scotch-tape method from the bulk of crystal hBN. However, the synthesis process usually requires a high pressure and high temperature and it take several days to prepare. During the growth, hBN powder was used as the precursor which dissolved in a liquid metal at high temperature, followed by the precipitation process during the cooling down process, which was under a certain cooling rate. For example, Taniguchi et al. demonstrated the synthesis of hBN single crystal at 4.5 GPa and at 1500°C using barium boron nitride (Ba₃B₂N₄). First, a hot-pressure hBN disc, was heated at 2100°C for 2 hours in a N₂ flow for removing oxygen residue. Since Ba₃B₂N₄ is hygroscopic and oxidises easily in air, the substrate together with the hBN power have to be synthesised and prepared in a dry N₂ atmosphere. The sample was encapsulated in a molybdenum (Mo) sample chamber inside a N₂-purged glove box in which O₂ and H₂O concentrations were kept below 1 ppm. Consequently, the sample was compressed between 4 and 5 GPa, and was heated between 1500°C and 1650°C. Growth times varied between 20 and 80 hours.
After the growth, the recovered Mo sample chamber was dissolved using hot aqua regia to obtain the crystals. Later, they found that Ni could serve to dissolve and precipitate h-BN, to form recrystallized h-BN.\textsuperscript{131} Ni is much less sensitive to the environment as compared to Ba\textsubscript{3}B\textsubscript{2}N\textsubscript{4}; however, high pressure (4.5-6 GPa) and high temperature (1300°C-1900°C) were still required for the growth process. In 2007, Kubota \textit{et al.} further improved the synthesis method by adding molybdenum (Mo) to Ni to increase the Ni solubility. The enhanced Ni solubility in the Ni-Mo system allows the recrystallization of large-area and high-quality hBN to occur under atmospheric pressure conditions.

![Diagram](image)

Figure 2.5 Segregation and precipitation method of preparing bulk hBN. (a) Segregation process from the solidified Ni-Mo liquid. Optical micrographs of recrystallized hBN obtained with a Ni-Mo liquid. (b) Typical hBN crystal on a solidified solvent (as grown). (c) Fragments of aggregated hBN crystals after acid treatment (the inset is an optical micrograph of the recovered sample). The shiny white regions are from reflection. (d) Cathodoluminescence spectra of the samples grown using an atmospheric pressure and high-temperature method (blue line), and grown by using a high pressure and high-temperature method (green line).\textsuperscript{132}

Recently, several groups have reported synthesis of hBN using the CVD method under atmospheric pressure or at low pressures. For example, Shi \textit{et al.} demonstrated
growth of hBN on a Ni substrate using borazine as the precursor. First, borazine forms polyborazylene upon deposition on polycrystalline Ni foil at 400°C in an ambient pressure of N₂. Consequently, an annealing process was performed to facilitate the dehydrogenation of the polyborazylene to yield hBN. (Figure 2.6) The thickness was dependent on the polyborazylene deposition time and the flow rate of borazine; a borazine flow rate of 1 sccm for 30 min and 10 sccm for 1 hour resulted in a final hBN thickness of 5 nm and 50 nm, respectively. Additionally, ammonia borane (NH₃-BH₃) was reported as the precursor to prepare monolayer to a few layer hBN film on Cu foil. Moreover, in their paper, Kim et al. found that by varying the sublimation temperature of ammonia borane and the growth time, the nucleation density and the thickness of the film can be controlled, which is important for applications such as the dielectric layer for graphene devices.

Figure 2.6 Schematic diagram of the hBN conversion process. The chemical structure of (a) polyborazylene, (b) dehydrogenation, and (c) recrystallization. (d) Growth procedure of hBN by using CVD with borazine. Each step is expected to have a corresponding conversion process.
Synthesis of monolayer hBN was also demonstrated on Ni(111)\textsuperscript{134}, Pd(111)\textsuperscript{135}, Ir(111)\textsuperscript{136} and other transitional metal substrates.\textsuperscript{137} However, the growth process requires expensive UHV chambers and the method does not allow scale-up production of the hBN.
Table 2.1 A summary of synthesis method for hBN.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Precipitation</th>
<th>CVD method</th>
<th>UHV method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrates</td>
<td>Barium boron nitride (Ba₃B₂N₄) and other transition metals or metal alloys (e.g., Ni, Ni-Mo, Ni-Cr)</td>
<td>Polycrystal transition metal foil including Cu, Ni and Pt</td>
<td>Single crystal transition metals such as Ni(111), Pd(111) and Ir(111)</td>
</tr>
<tr>
<td>Precursors</td>
<td>hBN powder</td>
<td>Borazine and ammonia borane</td>
<td>Borazine</td>
</tr>
<tr>
<td>Growth</td>
<td>Temp 1300 °C ~2000°C</td>
<td>800 °C ~1000°C</td>
<td>800 °C</td>
</tr>
<tr>
<td>conditions</td>
<td>Pressure ~4-6GPa</td>
<td>~1 Tor - atmospheric pressure</td>
<td>~10⁻⁸ Tor</td>
</tr>
<tr>
<td>Time</td>
<td>2-3 days</td>
<td>1-3 hours</td>
<td>The UHV condition takes time to reach, takes 1-2 days.</td>
</tr>
<tr>
<td>Film quality</td>
<td>High</td>
<td>Varies from different reports</td>
<td>High</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>Bulk</td>
<td>Monolayer to a few layers</td>
<td>Mostly monolayer, sometimes 1-2 layers</td>
</tr>
</tbody>
</table>
3.1 Preparation of Materials

3.1.1 Cu Foils for Bilayer Graphene

For bilayer graphene synthesis, the Cu foil (127 μm thick, 99.9%, product no. 13380) was purchased from Alfa Aesar. Before growth, the Cu foil was pretreated by dipping the foil into Ni etchant (nitric acid, Transene Company Inc.) for 30 s, followed by rinsing using deionized water. The enclosure was made by folding a 1 in. by 2 in. copper strip and crimping the edges using pliers. For experiments on studying the coverage dependence on the thickness of the Cu foil, we electro-chemically polished the Cu foil using phosphoric acid (85%, Macron) and deionized water mixture (volume ratio 3:1) as the electrolyte and with a bias of 2V.

It is important to note that the properties of bilayer graphene, in terms of coverage and domain size, are highly dependent on the shape, the impurity, and the roughness of the Cu foil, which is consistent with other reports.\textsuperscript{138-141} For example, high-coverage and large-size bilayer domains can be observed only using Cu enclosures with the edges tightly crimped. Using Cu enclosure without sealing at the edges leads to mostly monolayer graphene, which is similar to graphene growth on flat Cu foil.\textsuperscript{138} The sealing at the Cu enclosure is critical to the growth of bilayers because it creates two different growth environment where the CH\textsubscript{4} concentrations are different, resulting in different
growth rates. Furthermore, we found the purity of the Cu foil to play an important role in the nucleation density and the domain size of the resulting bilayers; when the purity is high (sample C in Table 3.1), there is no bilayer formation. In contrast, we found that foil with lower purity (Sample A in Table 3.1) favors multilayer growth. One possible explanation is that the impurities can enhance the catalytic activity; during the annealing, the impurities in the Cu foil diffuse to the surface, catalyze the carbon source at a higher rate that results in bilayers, or has a higher carbon solubility that later precipitates carbon. The certificates of chemical analysis for the Cu foils from Alfa Aesar can be found in the Appendix. However, the chemical analysis is not consistent. For example, the Cu foil with 99.9% purity have more impurities than that in Cu foil with 99.8% purites. Thus, a thorough charactarization of chemical composion should be performed and analyzed to investigate what elements are ciritical for facilitating bilayer growth. In addition, we found that there was less bilayer formation when we electro-chemically polish the Cu foil to smooth the surface. This finding is consistent with reports by other groups that electro-chemically polishing and many-hour annealing can help smooth the Cu surface in order to minimize the size and density of these bilayers. It is possible that carbon tends to accumulate at the step edges with lowered adsorption energy. However, in our experiment, bilayer formation is desirable. Therefore, if not specified, we did not use electro-chemical polishing methods. In the experiment where we needed to reduce the thickness of the Cu foil by electro-chemical polishing, a Kapton tape was used to cover one side of the Cu foil to preserve the surface properties.
Table 3.1 List of the Cu foils used for testing the growth of bilayer graphene and its as-received characteristics.

<table>
<thead>
<tr>
<th>Type</th>
<th>Vendor</th>
<th>Impurities</th>
<th>Types of impurities</th>
<th>As-received thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Alfa Aesar</td>
<td>99.8%</td>
<td>See Appendix</td>
<td>25 μm</td>
</tr>
<tr>
<td>B</td>
<td>Alfa Aesar</td>
<td>99.9%</td>
<td>See Appendix</td>
<td>127 μm</td>
</tr>
<tr>
<td>C</td>
<td>JX Metals and Mining (Japan)</td>
<td>99.99%</td>
<td></td>
<td>36 μm</td>
</tr>
</tbody>
</table>

3.1.2 Iron Foil and Platinum Foil for Hexagonal Boron Nitride

The Fe foil (100 μm thick, 99.99%, product no. 40493) and the Pt foil (100 μm thick, 99.997%, product no. 12059) were purchased from Alfa Aesar. Prior to the growth of hBN, the Fe foil was annealed at 1100°C for 1 hour to smoothen the surface under 200 sccm H₂ and 200 sccm Ar at atmospheric pressure. Then both surfaces of the Fe foil were electro-chemically polished for 2 min, respectively, using a mixture of glacial acetic acid (Amresco) and perchloric acid (Sigma-Aldrich) in a volume ratio of 7:3 with a bias of 30V. After polishing, the Fe foil was left in deionized water for sonication for 5 min, followed by rinsing using acetone and isopropyl alcohol (IPA). As for the Pt foil, we used a simple cleaning process by sonicating the Pt foil in acetone for 5 min, rinsing using acetone and IPA, and blow drying with nitrogen.
3.2 Furnace Design and the Growth Process

Bilayer graphene and hBN were synthesized in a single-zone hot-wall Lindberg/Blue M furnace. The size of the tube is 1 inch and therefore the substrates prepared in this experiment were about 1 by 1 inch. The simplified schematics of the setups for both bilayer graphene and hBN are shown in Figure 3.1. For bilayer graphene, CH₄ and H₂ gases were fed through mass flow controllers (MFC), which were connected to a home-made MFC controller. An additional ¹³CH₄ source was added to the graphene setup for studying isotopic labeling. In this thesis, ¹²CH₄ and ¹³CH₄ were sequentially introduced during the growth process; therefore, we did not need a setup to mix the ¹²CH₄ and ¹³CH₄ before the introduction of these gases.

For hBN growth, borazine (Gelest Inc.) was used as the precursor. A variety of precursors were reported for hBN growth including BF₃/NH₃, BCl₃/NH₃, and B₂H₆/NH₃. However, using these precursors needs to precisely control the ratio

Figure 3.1: Simplified schematics of the CVD setups for (a) bilayer graphene and (b) hBN.

For hBN growth, borazine (Gelest Inc.) was used as the precursor. A variety of precursors were reported for hBN growth including BF₃/NH₃, BCl₃/NH₃, and B₂H₆/NH₃. However, using these precursors needs to precisely control the ratio
between the boron source and NH$_3$ to obtain the stoichiometric ratio in hBN. Additionally, the deposition rate should be taken into consideration, which is also dependent on the amount of the precursors. In contrast, using single precursor are more advantageous over the mixture of two precursors since they show 1:1 B:N stoichiometric ratio. Such precursors include borazine (B$_3$H$_6$)$_6$, trichloroborazine (B$_3$H$_6$Cl$_3$), and hexachloroborazine (B$_3$N$_3$Cl$_6$). In particular, borazine is less toxic as compared to other boron containing precursors.

Since borazine is in liquid form at room temperature and has a high vapor pressure, it is stored in a commercial wine chiller kept at 3°C with a modified water cooling system. During the growth process, the borazine was bubbled and transported by a carrier gas (H$_2$ in this work) to the heating zone. Bubbling of the carrier gas through borazine allows for evaporation and ensures delivery of a constant amount of borazine into the reaction zone at a fixed temperature and flow rate. Moreover, during the growth, a cold trap was installed at the outlet to capture residual borazine or other products to prevent them from entering the vacuum pump.

### 3.2.1 Bilayer Graphene

For a typical bilayer graphene growth process, the Cu enclosure is placed in a quartz tube under 10 sccm H$_2$ at a pressure of 350 mTorr when the temperature ramps up to 1000 °C for 20 min. Then the substrate is annealed under the same condition for 30 min before we start to flow 1 sccm CH$_4$ and 50 sccm H$_2$. After growth, we turn off the furnace and the substrate is cooled in the same atmosphere.
The growth conditions listed above were optimized to produce large-domain and high-coverage bilayers graphene. It was reported that for monolayer graphene growth, high temperature, low CH$_4$ flow rate and low partial pressure are preferred for large-domain graphene.$^{118}$ Additionally, in our previous work, we found that the bilayers nucleate near the center of monolayer graphene.$^{138}$ Since the nucleation density of bilayers is highly correlated with that of the monolayer, in order to grow large-domain bilayers, we performed the growth at 1050°C, which is close to the melting temperature of Cu (1085°C).
Figure 3.3 Correlation of the nucleation density of monolayer and bilayer graphene. Top: from left to right, false-colored optical images of monolayer graphene flakes grown at 3 sccm CH4/50 sccm H2, 2 sccm CH4/50 sccm H2, and 1 sccm CH4/50 sccm H2 for 1 min. Bottom: from left to right, bilayer graphene grown under the same condition for 2 hours.

Figure 3.3 shows the graphene obtained from different gas compositions at 1050°C for different lengths of time. The figures above show graphene films that were prepared after 1 min growth; therefore, the film is not complete. We observed that the density of monolayer flakes decreases as the flow rate of CH4 decreases. As the growth time increases to 2 hours, we found that the bilayers prepared at low CH4 flow rate are larger. This is because bilayer nucleation sites, together with the monolayer domains, are more separated, allowing for larger domains.

3.2.2 Hexagonal Boron Nitride

The substrate was first annealed at 1100°C for 30 min under 30 sccm H2 before the borazine vapor (carrier gas flow rate: 0.1 sccm) and H2 (100 sccm) were introduced for different lengths of time for hBN growth. (Figure 3.4) A longer growth time leads to
thicker film, which will be discussed in detail in Chapter 4. After growth, a slow cooling rate (5°C/min) was applied until 700°C while the same gases were maintained. When the temperature reached 700°C, the furnace was opened and the tube was taken out for fast cooling. A similar growth parameter was used for hBN growth on Pt; however, the cooling rate is not critical in that case.

![Typical growth process used for hBN](image)

*The cooling rate depends on the substrate*

Figure 3.4 Typical growth process used for hBN, including annealing, growth and cooling.

The installation and operation of borazine as the precursor needs careful design. For instance, in Figure 3.5, the pressure at the gas source 1 (H₂ tank 1) is always higher than that at the gas source 2 (H₂ tank 2) to prevent the gas from pushing the liquid between H₂ tank 1 and H₂ tank 1 backward. (Figure 3.5) We also installed a check value (CV1) before gas source 1 for the same purpose. A second check value (CV2) was installed at the gas outlet near valve 5 (V5) to prevent air from entering the system. During the experiment, we found that if we used the setup for about three months, the MFC (mass flow controller) for borazine would get clogged. Therefore, we installed another line for purging the MFC after the growth. In Table 3.2, we summerize for
reference the condition of each valve during the growth process. The symbol O indicates that the valve is open and X means the valve is closed.

Figure 3.5 The schematics of the setup for the use of borazine as the precursor
Table 3.2 Summary of procedures for operating the valves for the use of borazine.

<table>
<thead>
<tr>
<th>Steps</th>
<th>Comments</th>
<th>V1</th>
<th>V2</th>
<th>V3</th>
<th>V4</th>
<th>V5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation</td>
<td>Flow gas through the borazine at 5 sccm, which is the maximum value of the MFC (mass flow controller). This procedure serves two purposes: (1) to purge the line; (2) to bubble the liquid precursor.</td>
<td>O</td>
<td>O</td>
<td>X</td>
<td>X</td>
<td>O</td>
</tr>
<tr>
<td>Before growth</td>
<td>After bubbling the borazine at a high flow rate, the precursor is ready for the growth of hBN. However, before the introduction of borazine into the hBN growth chamber, we purge the MFC immediately using H₂ at the same flow rate.</td>
<td>X</td>
<td>X</td>
<td>O</td>
<td>X</td>
<td>O</td>
</tr>
<tr>
<td>Growth</td>
<td>Flow carrier gas through borazine at 0.1 sccm.</td>
<td>O</td>
<td>O</td>
<td>X</td>
<td>O</td>
<td>X</td>
</tr>
<tr>
<td>After Growth</td>
<td>When the system is idle, we always flow gas through the MFC at 5 sccm for keeping the MFC clean.</td>
<td>X</td>
<td>X</td>
<td>O</td>
<td>X</td>
<td>O</td>
</tr>
</tbody>
</table>

3.3 Transfer Techniques

In this section of the thesis, we aim to discuss the transfer process of bilayer graphene and hBN. To achieve this objective, we first discuss the transfer process for graphene which guided our method that produced a successful transfer of graphene on Cu foil to a target substrate. Then we discuss how this process was modified to achieve a transfer process for hBN.
3.3.1 Wet Transfer for Bilayer Graphene and Hexagonal Boron Nitride

The wet transfer of both bilayer graphene and hBN involves the removing of the underlying metal substrate using acid as the etchant. To transfer graphene, we coated the graphene on Cu with a layer of poly(methyl methacrylate) (PMMA, 950 A9, MicroChem, diluted to 4.5% in anisole) at 2500 rpm for 1 min. After coating, we placed the sample in an oven at 80°C for 10 min. The Cu foil was then removed by floating the coated sample on a Cu etchant (CE-100, Transene Company Inc.) for 1 hour. Subsequently, we washed the PMMA/graphene and transferred PMMA/graphene onto a target substrate. The target substrate could be a bare SiO₂/Si substrate, a patterned SiO₂/Si substrate with trenched features or Au pads, or a TEM grid. The PMMA was removed by acetone, followed by 3 hr thermal annealing at 350°C under a mixture of 200 sccm H₂ and 200 sccm Ar at atmospheric pressure. The wet transfer process was similar for hBN grown on Fe. Instead of Cu etchant, we used nitric acid (Transene Company Inc.) to dissolve the Fe substrate.

Figure 3.6 Schematics of graphene transfer using a wet etching.
3.3.3 Bubble Transfer for Hexagonal Boron Nitride

In this thesis, we used a bubble transfer method to transfer hBN from the Pt foil to a SiO₂/Si substrate in order to recycle the substrate. First, we coated the hBN on Pt with a layer of PMMA (PMMA, 950 A9, MicroChem, diluted to 6.75% in anisole) at 2500 rpm for 1 min. It should be noted that the PMMA layer for a bubble transfer was thicker than that used for wet etching. After baking in an oven at 80°C for 10 min, the PMMA/hBN/Pt sandwich was then fully immersed in an aqueous solution of 1 M NaOH as a cathode. (Figure 3.7) The top part (1 cm by 0.3 cm) was left in air for electrical condution with the wire. A Pt mash was used as an anode. When a bias of 3 V was applied, H₂ bubbles were generated, dislodging the full PMMA/hBN layer off the substrate. After the PMMA/hBN was completely delaminated from the Pt foil, the voltage was turned off. The floating PMMA/hBN was then transferred to deionized water for three times to remove the residual NaOH solution before it was picked up by the designated substrates such as SiO₂/Si chips or TEM grids.

Figure 3.7 Schematics of the bubbling transfer setup and process.⁷⁴
3.4 Characterization Methods

3.4.1 Optical Microscopy and Scanning Electron Microscopy

3.4.1.1 Bilayer Graphene

Optical microscopy and scanning electron microscopy (SEM) were used to image the graphene after growth. Using the contrast in the optical images and SEM images to identify the number of graphene layers has been discussed in many literatures.\textsuperscript{111, 151, 152} Nevertheless, for our CVD-grown sample, monolayer and bilayers, or monolayer, bilayers and trilayers are present in one sample at the same time; therefore, we can easily differentiate the number of layers by the increasing contrast. For example, figure 3.8 (a) shows an optical image of a transferred graphene film on the SiO\textsubscript{2} (300nm)/Si substrate, while Figure 3.8 (b) shows the corresponding SEM image. The prepared graphene is not complete; therefore, the lighter background in both of the images represents the substrate. The flakes with size of \(\sim 10\ \mu m\) are discrete monolayer flakes. The darker regions near the center of graphene flakes are the bilayer domains.

![Figure 3.8](image)

(a)  
(b)  

10 \(\mu m\)  
10 \(\mu m\)

Figure 3.8 (a) Optical images and (b) SEM images of incomplete graphene after growth.

Usually SEM was used first for the direct examination of the graphene nucleation density and the size of bilayers on the Cu foil after growth. However, the contrast of
bilayers on the complete monolayer graphene varies a lot, depending on the grain orientations of the Cu foil, as shown in Figure 3.9 (a) and (b). Thus, for calculating the coverage of bilayers, we transferred the graphene film onto SiO$_2$ (300nm)/Si for optical imaging (Figure 3.9 (c)). For a better contrast, we use false-colored images where different number of layers were represented by different shades of pink. The detailed steps for false-coloring processes are described in the Appendix. As shown in Figure 3.9 (d), the lightest pink represents the first layer. The darker regions are bilayers whereas the darkest pink regions are trilayers.

Figure 3.9 Complete monolayer graphene with bilayer domains. (a),(b) SEM images of graphene across different Cu grains. (c) Optical images of graphene on SiO$_2$/Si. (d) False-colored images of (c).
3.4.1.2 Hexagonal Boron Nitride

In the case of graphene, the number of layers - monolayer, bilayers and trilayers - can be easily identified by their optical contrast. However, for hBN, there is little contrast in the optical contrast due to the large band gap. Even after using the SiO$_2$ (285nm)/Si for the interference enhancement (Figure 3.10), one layer of hBN thin film only show white-light contrast of less than 1.5%, which is hard to detect by naked eyes. Thus, optical imaging is not a reliable way for identifying the number of hBN layers.

Figure 3.10 Optical images of (a) monolayer hBN (b) bilayer hBN and (c) trilayer hBN thin films. The substrate is SiO$_2$(285nm)/Si. Courtesy of Joel Wang from Harvard University.

Figure 3.11 shows an optical image of a transferred thick hBN film on SiO$_2$/Si substrate. The thick hBN film was prepared on Fe. In contrast to graphene, for which the number of layers can be precisely determined using optical reflection measurement, it is hard to quantify the number of layers of hBN solely from the optical images.
For charactering hBN films, we also used SEM for directly imaging the morphologies of as-grown films such as thickness and the shape. Figure 3.12 shows a SEM picture of hBN on Fe substrate after growth of 0.2 sccm H\textsubscript{2} carrier gas and 100 sccm H\textsubscript{2} at 1100°C for 3 hours. The triangles and hexagons are thick hBN regions with more than 20 layers of hBN films stacked in a pyramid structure. However, SEM cannot be used to differentiate the number of layers.
3.4.2 Raman Spectroscopy

3.4.2.1 Bilayer Graphene

Raman Spectroscopy is a widely used non-destructive tool for characterizing graphene. Although there are many papers reporting the physics and identifications of various phonon modes associated with graphene, in most basic cases, three peaks are conventionally used for a rapid characterization of the quality of graphene, such as the crystallinity and the number of layers. The peaks are labeled G, G' and D. The G peak at ~1580 originates from a first-order Raman-allowed scattering process and corresponds to the in-plane, doubly degenerate phonon mode with $E_{2g}$ symmetry. The G' and D modes come from a second-order double resonance process between non-equivalent K points in the Brillouin zone of graphene, involving two phonons for the G' and one phonon and a defect for the D band. (Figure 3.13)
Figure 3.13 First-order G band process (Left), one-phonon second-order process for the D band (top) and the D' band (bottom), two-phonon second-order resonance Raman spectral processes for the double resonance G' process (top) and for the triple resonance G' band.\textsuperscript{158}
Figure 3.14 Raman spectra taken from CVD-grown graphene films. Monolayer graphene (black), turbostratic bilayers (green) and AB-stacked bilayers (blue).

Figure 3.14 shows typical Raman spectra for monolayer graphene and bilayers graphene. The D peak (~1350 cm\(^{-1}\)), which is associated with the defects, such as lattice defects\(^\text{159}\), were usually absent for samples prepared in this thesis (unless the D band was intentionally created), indicating high quality graphene films. The peak at ~1580-1600 cm\(^{-1}\) is the G peak. This peak is also sensitive to the chemical doping in graphene: excess carriers in graphene can result in a shift in the peak position of the G peak.\(^\text{157}\) The G’ peak located at ~2660-2680 cm\(^{-1}\) also can be used to study the doping level. Moreover, the full width at half maximum (FWHM) of the G’ peak can be used for identifying the amount of turbostratic and the amount of AB-stacked bilayer graphene. For turbostratic bilayers, the interaction between the two layers is weak so that their Raman spectra resemble the Raman spectra of monolayer graphene, despite the fact that the absolute intensity of the spectra approximately doubles. Furthermore, there are many papers
reporting the angle-dependent Raman features on the rotational angles.\textsuperscript{160, 161} For AB-stacked bilayers, because of the splitting of the phonon branches and of the electronic bands, there are four possible double resonance processes contributing to the $G'$ band at ~2700 cm\textsuperscript{-1}.\textsuperscript{162} Thus, the relative intensities and the linewidth as well as the absolute intensitives rely on evaluating the asymmetry or the FWHM of the $G'$ Raman peak. However, for CVD-prepared graphene samples, distinguishing the stacking order requires fitting four Lorentzian peaks but such results can be ambiguous especially since the asymmetry of the $G'$ band is usually absent. To calculate the percentage of AB-stacked bilayers, Raman mapping was performed and the FWHM were plotted in the histogram. Then the authors need to define a cut-off value (usually from 45 cm\textsuperscript{-1} to 60 cm\textsuperscript{-1}) for the AB-stacked bilayers.\textsuperscript{79, 163} The final percentage is dependent on the value chosen and can vary between papers. Therefore, we need a better method of identifying the percentage of AB-stacked regions more rapidly and accurately.

It it worth mentioning that isotopic labeling (\textsuperscript{12}C and \textsuperscript{13}C) combined with Raman spectroscopy have been effective in precisely tracking the amount of deposited carbon during the growth process of graphene. Due to the different masses of the \textsuperscript{12}C and \textsuperscript{13}C atoms, the corresponding phonons observed in the \textsuperscript{12}C and the \textsuperscript{13}C graphene layers differ in energy (frequency).\textsuperscript{164} Therefore, the Raman spectrum of the \textsuperscript{13}C monolayer sample exhibits the same Raman features as that of the \textsuperscript{12}C monolayer except for a downshift of all the Raman peaks. (Figure 3.15) The frequency shifts of the Raman peaks in a \textsuperscript{13}C enriched graphene sample with respect to the \textsuperscript{12}C counterpart can be calculated by equation

$$\omega = \omega_{12} \sqrt{\frac{m_{12}}{n_{12} m_{12} + n_{13} m_{13}}}$$  \hspace{1cm} \text{Eq. (3.1)}
where \( \omega_{12} \) is the frequency of a particular Raman spectrum of the \(^{12}\text{C}\) sample, \( n_{12} \) and \( n_{13} \) are the atomic fractions, and \( m_{12} \) and \( m_{13} \) are the atomic masses of \(^{12}\text{C}\) and \(^{13}\text{C}\), respectively.\(^{109,165}\)

![Figure 3.15 Raman spectra of \(^{12}\text{C}\) monolayer graphene (black) and \(^{13}\text{C}\) monolayer graphene (red).](image)

Li et al. used isotope labeling to investigate the growth mechanism of graphene on Ni and Cu. In their experiment, \(^{12}\text{CH}_4\) and \(^{13}\text{CH}_4\) gases were sequentially introduced into the chamber for 1 min for several cycles. Then, the distribution of carbon isotopes in the resulting graphene were plotted by Raman mapping on both of Ni and Cu substrates. On Ni, the Raman mapping of the intensities of both \(^{12}\text{C}\) and \(^{13}\text{C}\) shows a randomly mixed composition of isotopes, with broad Raman peaks and with frequencies in the middle of those expected for pure \(^{12}\text{C}\) and \(^{13}\text{C}\) graphene, suggesting a segregation and a precipitation process. (Figure 3.16 (a)) In contrast, for graphene grown on the Cu substrate, it shows distinguishable pure \(^{12}\text{C}\) and pure \(^{13}\text{C}\) regions, with spatially resolved quasi-concentric areas formed only by one of the isotopes (Figure 3.16 (b)), indicating a surface-catalytic process. The red-filled area corresponds to the center of the individual grain, where the growth was initiated, the composition is pure \(^{13}\text{C}\). After 1 min, \(^{12}\text{C}\) came
to contribute to the graphene formation, which is reflected by the black ring surrounding the red areas. This method allows us to view the grain size distribution directly in a mapping. Tracing all the parameters while varying the growth conditions and the growth time can help us understand the process of the growth.

![Schematic diagrams](image)

Figure 3.16 Schematic diagrams of the possible distribution of carbon isotopes in graphene films based on different growth mechanisms for sequential input of carbon isotopes. (a) Graphene with randomly mixed isotopes such as might occur from surface segregation and/or precipitation. (b) Graphene with separated isotopes such as might occur by surface adsorption.¹⁰⁹

### 3.4.2.2 Hexagonal Boron Nitride

Raman spectroscopy is an effective and high-throughput method for determining the number of hBN layers up to 3 layers. Figure 3.17 shows representative Raman spectra of bulk hBN, mono-, bi- and tri- layers of hBN thin films. As the layer numbers increases, the intensity increases. For bulk hBN, the characteristic hBN peak is located at ~ 1366 cm⁻¹.¹⁶⁶ In contrast, the peak for monolayer show a blue shift by ~4 cm⁻¹, contributing to a hardening of the E₂g phonon mode from a slightly shorter B-N bond in
isolated monolayers. For bilayer hBN, there is a 1 to 2 cm\(^{-1}\) red shift, resulting from the random strain induced probably during the cleavage. Figure 3.17(b) shows the position of the hBN peak for different number of layers. During our experiment, we found the location of the peak varies, consistent with the report. However, the shape and the intensity of the peaks are always the same; therefore, we use these two characteristics for determining the layer numbers of hBN.

![Raman spectra of hBN thin film with different number of layers.](image)

Figure 3.17 Raman spectra of hBN thin film with different number of layers. (a) Raman spectra of atomically thin BN. The left inset shows changes in integrated intensity with the number of layers. The right picture illustrates the phonon mode responsible for the Raman peak. (b) Position of the Raman peak for different number of layers. In mono- and bi-layer hBN, the peak position is sample dependent and varies by as much as ± 2 cm\(^{-1}\). The dashed line is the Raman shift predicted for monolayer hBN. The error bar indicates a typical accuracy of determining the peak position using our spectrometer.
3.4.3 List of the Equipment and Materials Used

Raman mapping was performed in a home-built Raman system with a X-Y motorized microscope stage taken with a Nd:YAG laser at 532 nm at a power of ~1-2 mW using a 100x objective with a beam spot size of ~1 µm. The data were then processed with automated Lorentzian fitting in MATLAB.

Selected area diffraction patterns (SAED) were taken using a JEOL 2011 TEM at 120 kV. High-resolution images were performed using a JEOL 2010F TEM instrument to measure the structure.

X-ray photoelectron spectroscopy (XPS) was performed using a PHI Versaprobe II.

X-ray diffraction (XRD) was performed using a Panalytical Multipurpose Diffractometer with Cu $K_{\alpha}$ radiation. SEM images were taken using a FEI Helios 600i.
Chapter 4: Synthesis and Characterization of Bilayer Graphene

Chapter 4 describes the synthesis of bilayer graphene and the techniques developed to investigate its growth mechanism. We will begin by demonstrating that the high-coverage large-domain bilayer graphene can be synthesized when using the Cu enclosure method. By isotopically labeling the graphene during the growth process, bilayer graphene with $^{12}$C- and $^{13}$C-labeled layers can be prepared. Such samples allow us to provide a facile identification of the stacking orientation using Raman spectroscopy. Moreover, by combining surface sensitive fluorination with such hybrid $^{12}$C/$^{13}$C bilayer samples, we are able to identify that the second layer grows underneath the first-grown layer. Then, we further investigate the growth mechanism of the bilayer graphene on the outside surface of Cu enclosures at low pressures. We found that the carbon diffuses from the inside to the outside of the enclosures to form bilayers via the exposed Cu regions and thus we were able to develop a method to precisely control the number of directly synthesized graphene layers. Lastly, by controlling the carbon diffusion process, we prepare large-domain (>200 μm) monolayer graphene that is free of any bi-/multi-layers by using Cu double enclosures. These advances are discussed in this chapter.
4.1 Identification of the Stacking Orientation

Identifying the stacking orientation of bilayers is crucial for its application, hence the electronic structures are dependent on the rotational angles. There are many methods for charactering the stacking orientation. The most commonly used methods include Raman spectroscopy and SAED. These methods generally rely on evaluating the FWHM of the G' Raman peak combined with SAED patterns to verify the stacking orientation. However, SAED is a time consuming process and only examines a relatively small sample region and the Raman spectra do not always provide a clear signature for identifying the type of bilayer stacking. Therefore, finding an efficient and confident method to identify the stacking orientation and to assess the area percentage of AB-stacked bilayer versus turbostratic bilayer in a graphene sample will be beneficial for the controlled synthesis in the future.

4.1.1 Synthesis of Bilayer Graphene on Cu Enclosures

Cu enclosures were utilized for the growth of large-domain bilayer graphene by the LP (low pressure) CVD. The Cu enclosure method was initiated by Li et al. for the synthesis of large single-crystalline domain graphene flakes. It has been found that this geometry also favors the growth of bilayer graphene. Figure 4.1 (a) shows the Cu enclosure, and Figure 4.1 (b) shows the CVD system used in this experiment. After growing at 1050°C under 1.5 sccm CH₄ and 50 sccm H₂ for 1 hour, the Cu enclosure was opened (Figure 4.1 (d)), and graphene domains could be observed on both the outside and the inside surfaces by SEM, as shown in Figure 4.1 (c) and (e), respectively. Hexagonal bilayer domains of approximately 20 μm on the complete monolayer background were observed on the outside surface, while large-area (up to hundreds of micrometers) discrete dendritic monolayer flakes were found on the inside surface. Here we have
focused on the outside surface due to the higher bilayer graphene coverage that was observed on the outside surface.

Figure 4.1 Cu enclosure and graphene grown on the Cu enclosures. (a) Photograph of a Cu enclosure. (b) Illustration of the CVD system with the Cu enclosure in the center of the heating zone. (c) SEM image of the outside surface of a Cu enclosure, where some of the hexagonal bilayer graphene domains are outlined by the white dotted line. (d) Photograph of an open Cu enclosure after growth. (e) SEM image of the dendritic monolayer graphene flakes on the inside surface of a Cu enclosure, where an isolated dendrite is outlined by the white dotted line, to show an example of a typical dendrite.

To study the growth effect of the Cu enclosure on bilayer graphene, graphene films on flat and enclosed substrates were grown side by side at 1000°C using 1.5 sccm CH₄ and 35 sccm H₂ for different lengths of time. In Figure 4.2, the SEM images show that in the early growth stages (within the first 5 min), the monolayer graphene coverage was not complete. In the center of the individual graphene domains, we observed darker regions, which correspond to bilayer or multi-layer graphene. We found that these bilayer or multi-layers nucleate at the same time as the monolayer graphene. In addition, at this early stage (~ 5 min) the nucleation density and the size of the bilayer graphene domains were similar on both flat and enclosed substrates. As the growth progresses further,
individual monolayer graphene domains coalesced into a single monolayer. It should be noted that once the monolayer coverage was complete, we observed a “self-limiting” effect for the growth rate of the bilayer graphene on the flat substrate, consistent with previous reports. On the other hand, under this same condition, bilayer graphene on the outside of the Cu enclosure overcame the “self-limiting” effect and continued to grow until the bilayer growth finally saturated at about 70% total coverage on the outside surface of the Cu enclosure.

Figure 4.2 Comparison of graphene film growth as a function of time. Samples were imaged on both flat Cu substrates and on the outside surface of Cu enclosures at 1000°C using 1.5 sccm CH₄ and 35 sccm H₂ for the growth conditions. The SEM images all have the same magnification (10 kx) and the scale bars are all 10µm.

4.1.2 Raman and TEM Characterizations and Studies

Using the same enclosure method, we sequentially controlled the introduction of ¹²C and ¹³C in order to grow ¹²C/¹³C hybrid bilayer graphene. We introduced ¹²CH₄ for 90 seconds to grow the continuous monolayer and then purged the system for 5 minutes with 100 sccm Ar / 10 sccm H₂ to reduce intermixing between the isotopes. After purging, we introduced ¹³CH₄ for 30 minutes to increase the domain size of the bilayer. Figure 4.3 (a)
shows the optical images of the transferred bilayer graphene grown on the outside of the Cu enclosure using 1.5 sccm CH$_4$/ 50 H$_2$ at 1035°C. Figure 4.3 (b) shows a two-dimensional Raman map showing the integrated G peak intensity of $^{12}$C (1580-1620 cm$^{-1}$) and $^{13}$C (1510-1550 cm$^{-1}$), respectively. In the G peak mapping for $^{12}$C, we observed that the monolayer graphene is continuous and composed entirely of $^{12}$C. The higher G peak intensity regions in the center corresponds to $^{12}$C/$^{13}$C bilayer, which nucleated with the monolayer domain at the same time as shown previously in Figure 4.2. In the G peak mapping for $^{13}$C, the bright regions show the distribution of $^{13}$C while the black regions indicate the absence of $^{13}$C. After the first 90 seconds of growth using $^{12}$CH$_4$ and purging, the $^{13}$CH$_4$ decomposed and attached to the edges of already existing hexagonal bilayer graphene domains.

Figure 4.3(c) presents the typical Raman spectra taken from different locations in Figure 4.3 (b). To differentiate between various stacking orientations and layers, we adopt a naming convention consisting of [Isotope Stacking orientation-Number of layers]; for example, $^{12}$C/$^{13}$C AB-BLG denotes AB-stacked bilayer graphene composed of $^{12}$C only. In Figure 4.3(c), the black spectra show the reference monolayer spectra of $^{12}$C and $^{13}$C. The Raman spectrum of the $^{13}$C monolayer graphene ($^{13}$C SLG) exhibited a downshift of all the Raman features compared to the $^{12}$C monolayer graphene ($^{12}$C SLG), due to the different phonon energies resulting from the different $^{12}$C and $^{13}$C masses.$^{164}$ The blue spectra in Figure 4.3 were taken from the center of the two bilayer domains, which are composed of $^{13}$C only. The dotted blue-line spectrum exhibits a G' peak with a FWHM of ~28 cm$^{-1}$ and a G'/G peak intensity ratio of ~6.2, suggesting it is a turbostratic bilayer system. On the other hand, the solid blue-line spectrum exhibited a G' peak with a FWHM of ~64 cm$^{-1}$ and a lower G'/G intensity ratio of ~1.56. This strongly suggested the occurrence of AB stacking, even though some of the common features and asymmetries in the spectrum were not as clear as the ones observed in exfoliated Bernal AB-stacked graphene. Finally, the red spectra were taken from the outer region of the
bilayer domains where each layer was solely composed of $^{12}$C or $^{13}$C. Both spectra showed a clear separation of the G peaks associated with each C isotope at 1523 cm$^{-1}$ and 1588 cm$^{-1}$ - a superposition of one $^{12}$C layer and another $^{13}$C layer. However, while both red spectra clearly showed two types of graphene, the shape of their G' peaks differed significantly. The dotted red-line spectrum from the turbostratic bilayer graphene sample shows two distinct G' bands, which is to be expected for two electronically decoupled layers, while the solid red-line spectrum shows only a singular, but broader G' band with a FWHM of ~106 cm$^{-1}$, almost twice the FWHM observed for the $^{12}$C/$^{12}$C AB-BLG. We attribute this broad G' band to an interlayer interaction, which appears due to a similar stacking as observed by the Raman spectra of $^{12}$C/$^{12}$C AB-BLG in the center.

Figure 4.3 Raman spectroscopy and TEM characterization of bilayer graphene. (a) Raman spectra of $^{12}$C monolayer and $^{13}$C monolayer (black), $^{12}$C/$^{12}$C turbostratic bilayer (dotted blue), $^{12}$C/$^{12}$C AB-stacked bilayer (solid blue), $^{12}$C/$^{13}$C turbostratic bilayer (dotted red) and $^{12}$C/$^{13}$C AB-stacked bilayer (solid red) taken from (b). (b) Optical image of bilayer graphene transferred on Si/SiO$_2$. Scale bar is 5μm. The bilayer domain outlined
by the purple dots is AB-stacked and another domain by orange is turbostratic. (c) Integrated G peak intensity of $^{12}\text{C}$ (1580-1620 cm$^{-1}$) or $^{13}\text{C}$ (1510-1550 cm$^{-1}$), respectively, for domains in (b).

TEM and SAED were used to further confirm the stacking orientation of the graphene bilayers. The TEM and SAED sample was prepared by transferring graphene films grown under the same conditions as the Raman samples discussed above onto SiN TEM substrates. We chose silicon nitride TEM substrates instead of quantfoil TEM grids because the silicon nitride membrane is more rigid than the carbon film. This approach was adopted because we found that some important regions of the sample were not in focus using quantfoil TEM grid for the Raman mapping. A schematic of the transferred samples on a SiN TEM grid is shown in Figure 4.4.

![SEM image of transferred graphene on SiN TEM grid]

Figure 4.4 SEM images and schematics of transferred graphene on the silicon nitride TEM grid. The black dots are empty regions without graphene while white dots are holes with graphene films covered. The 20 μm scale bar on the SEM image should be noted.
After graphene was transferred onto the silicon nitride TEM grid, we first scanned the whole surface under SEM to find regions with more complete suspended bilayers. Then, Raman mapping was performed on the same locations. Regions (holes) with either separated $G'$ peaks or a broader $G'$ peak were recorded and each spectrum was plotted for later SAED reference. For example, all spectra show two $G$ peaks, indicating hybrid $^{12}\text{C}-^{13}\text{C}$ bilayer regions. In particular, spectra from locations 1, 5, 7 show distinct $G'$ peaks while those from the rest of the locations exhibit a combined $G'$ peak. (Figure 4.5)

![Figure 4.5 Characterization of graphene on a silicon nitride TEM grid. (a) SEM of graphene on the TEM grid. (b) Corresponding Raman mapping of the $G$ peak position at the same location. The holes indicates the broken regions. The red circle marks the center of the mapping. (c) Illustrations of the eight mapped regions, each indicated by a number. (d) Raman spectra taken from each of the regions labeld in (c). The numbers show the locations.](image-url)
Following Raman mapping, we then carried out SAED (Selected area electron diffraction) measurement at more than 50 different locations according to the Raman spectra and found a correlation between Raman and TEM. Examples are shown in Figure 4.6. For a Raman spectra with two distinct G’ bands; the electron diffraction pattern always generates two sets of monolayer graphene diffraction patterns. By examining the intensity profile of the diffraction spots, we learned that the bilayers were composed of two monolayers of turbostratic graphene. In contrast, for a broad G’ Raman spectra, only a single diffraction pattern was observed. Plotting the line intensity of the diffraction peaks, we found that the ratio of intensity of the equivalent planes \{1-210\} over the inner peaks from \{1-100\} is about 2, which confirms AB stacking.

![SAED analysis of the stacking orientation in bilayer graphene. Two representative Top: Raman spectra taken from suspended bilayer graphene on a silicon nitride TEM grid. The insets show the stacking orientation. Bottom: the SAED patterns for and the corresponding intensities profile along the yellow lines.](image)
Figure 4.7 Raman spectra taken from suspended bilayer graphene on a silicon nitride TEM grid. The insets show the corresponding SAED patterns and the angle between two layers.

Figure 4.7 shows the twisting angles between two layers of graphene and the corresponding Raman spectra taken at different locations. For turbostratic bilayers, there are two sets of patterns and the numbers indicate the rotational angles between the two layers. We found that the distribution of the twisting angles is random, which does not appear to have any angular preference.
4.1.3 Raman Analysis

To explain the origin of the broad G' band for $^{12}$C/$^{13}$C AB-BLG, we must first understand the phonon structure changes in $^{12}$C/$^{12}$C AB-BLG. In SLG, we have two carbon atoms in the unit cell, which gives us six phonon branches. Three of them are acoustic modes and another three are optical modes, which are labeled as iTO (in-plane transverse optical mode), LO (in-plane longitudinal optical mode) and ZO (out-of-plane transverse optical mode). The ZO mode is not Raman-active in SLG systems. Around the high-symmetry Γ point, the iTO and LO modes are degenerate and describe the G-band Raman peak, appearing around 1585 cm$^{-1}$, while around the high-symmetry K point the iTO mode describes the G' Raman feature (the G' peak is a double phonon resonant Raman process involving two iTO phonons around the K point). In the case of BLG, the unit cell has four atoms and, therefore, 12 phonon modes. If no interlayer interactions take place, the six phonon modes of the bottom layer are completely degenerate with the six phonon modes of the top layer in this two-layer system.

However, the AB-BLG system can be understood as a weak coupling between the six phonon modes of the bottom layer and the six phonon modes of the top layer. The main consequences of this coupling are: (1) the double-degenerate iTO/LO phonon branch around the Γ point, which describes the G band feature, evolves into two doubly-degenerate sets, whose frequencies are expected to split apart by less than 2 cm$^{-1}$. In most cases, the value is too small to be observed; (2) new Raman modes related to the breathing of the graphene layers are now observed and; (3) due to symmetry arguments, the iTO branches from the top and bottom layer are still degenerate around the K point. Given that the iTO phonons are degenerate (in $^{12}$C/$^{12}$C AB-BLG), the G' line shape for an AB-BLG system is quite distinct. It is because even though the iTO modes are degenerate at the K point, the interlayer interactions transform the doubly-degenerate linear electronic dispersion (around the K point) in a $^{12}$C/$^{12}$C t-BLG into a hyperbolic dispersion.
with two different sub-bands (around the $K$ point) in a $^{12}\text{C}/^{12}\text{C}$ AB-BLG. As largely discussed in the literature,\textsuperscript{158} for $^{12}\text{C}/^{12}\text{C}$ AB-BLG, the $G'$ feature is shown to be comprised of four peaks due to different resonances of the iTO mode with the different electronic sub-bands, as shown in Figure 4.8.

Figure 4.8 Raman signatures for the AB-stacked BLG structures. Raman signatures for the AB-stacked BLG structures. (a) Double resonance Raman processes which give rise to the four peaks in the $G'$ band in AB-BLG obtained from HOPG. The inset shows the $G'$ band measured with the 532nm laser line and the four peaks corresponding to each resonance process: $P_{11}$ (black line), $P_{12}$ (red line), $P_{21}$ (green line) and $P_{22}$ (blue line), with the relative magnitudes of the four phonon wavevectors $q$ shown. (b) Peak fitting of the $G'$ band for $^{12}\text{C}/^{12}\text{C}$ AB-BLG (AB-stacked bilayer graphene), $^{13}\text{C}/^{13}\text{C}$ AB-BLG, and $^{12}\text{C}/^{13}\text{C}$ AB-BLG. As expected, the $G'$ FWHM for the $^{12}\text{C}/^{13}\text{C}$ AB-BLG sample is almost twice the $G'$ FWHM of the $^{12}\text{C}/^{12}\text{C}$ AB-BLG and $^{13}\text{C}/^{13}\text{C}$ AB-BLG samples.

These arguments are further extended to the $^{12}\text{C}/^{13}\text{C}$ BLG system. In the case of the $^{12}\text{C}/^{13}\text{C}$ t-BLG system, we still have the six phonon modes of the bottom layer and the six
phonon modes of the top layer. However, the phonon modes are no longer degenerate (the degeneracy is broken due to the different masses of the carbon isotopes), but their electronic dispersions are kept linear (Dirac-like dispersion) and independent, and therefore they vibrate with frequencies which are related by

$$\omega(^{13}C) = \sqrt{\frac{12}{13}} \omega(^{12}C)$$  \hspace{1cm} \text{Eq. (4.1)}$$

where $\omega(^{13}C)$ and $\omega(^{12}C)$ denote the phonon mode frequencies in the $^{13}$C and $^{12}$C layers, respectively. This fully explains the consistent shifts in the system $^{12}$C/$^{13}$C t-BLG. For a $^{12}$C/$^{13}$C AB-BLG system, we still will observe two G band features (a first order Raman process around the $\Gamma$ point), since the different phonons due to their masses play a larger role than the change in electronic dispersion. However, for the G' band, the situation is slightly different because due to the differences in the $^{12}$C and $^{13}$C masses, the iTO modes from the top and bottom layers are no longer degenerate at the K point. However, similar to what happens for the $^{12}$C/$^{12}$C AB-BLG system, the electronic dispersion is still a hyperbolic dispersion with two different sub-bands (around the K point), since in this isotopic system, opposite to what happens to the vibrational properties, the electronic properties are maintained. Therefore, instead of four resonances with the iTO mode, we could observe up to eight different resonances, in which each resonance, as shown in Figure 4.8.

Indeed, only the energy of the iTO phonon mode will change with changing the mass between the $^{12}$C and the $^{13}$C carbon isotopes. Their phonon dispersions (in other words, the way the phonon frequency changes with changing the phonon momentum) will be the same, since this is determined by the electronic interactions of the system. This explains why the FWHM observed in the G' for the $^{12}$C/$^{13}$C AB-BLG system is almost twice the FWHM observed for $^{12}$C/$^{12}$C AB-BLG systems.
In order to enforce our arguments, in Figure 4.8 (b), we fit the G' band of $^{12}\text{C}/^{12}\text{C}$ AB-BLG and $^{13}\text{C}/^{13}\text{C}$ AB-BLG using four Lorentzian peaks (in a process similar to that shown in Figure 4.8 (a)) corresponding to the four allowed transitions, each with an individual FWHM of 36.3 cm$^{-1}$ and 32.1 cm$^{-1}$, respectively. These linewidth are in good agreement with the values found for exfoliated $^{12}\text{C}/^{12}\text{C}$ AB-BLG samples. Likewise, we fit eight peaks to the G' peak in the $^{12}\text{C}/^{13}\text{C}$ AB-BLG. Table 4.1 includes all fitted peak positions. The peak positions and FWHM (32.1 cm$^{-1}$) of the eight fitted peaks are quite similar to the individual $^{12}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{13}\text{C}$ fitted values. This suggests that, even though the coupling between layers is relatively weak in the $^{12}\text{C}/^{13}\text{C}$ AB-BLG (such that it does not perturb the original phonon modes very significantly), this coupling is sufficient to generate a hyperbolic electronic dispersion similar to that of $^{12}\text{C}/^{12}\text{C}$ AB-BLG or $^{13}\text{C}/^{13}\text{C}$ AB-BLG samples so that the multiple resonances can be observed.

Table 4.1 Information on the fitting of bilayer graphene for Figure 4.8 (b).

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<th>FWHM</th>
<th>$^{13}\text{C}/^{13}\text{C}$ AB-BLG (cm$^{-1}$)</th>
<th>Peak position</th>
<th>FWHM</th>
<th>$^{12}\text{C}/^{13}\text{C}$ AB-BLG (cm$^{-1}$)</th>
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<th>FWHM</th>
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<td>6</td>
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<td>2589.5</td>
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<td>2564.9</td>
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The stacking orientation in the $^{12}\text{C}/^{13}\text{C}$ AB-BLG systems was also confirmed by the observation of interlayer breathing modes, as shown in Figure 4.9. In $^{12}\text{C}/^{12}\text{C}$ AB-BLG, it is already well established that the combination of modes LO+ZO' and 2ZO appearing in the frequency range from 1650 to 1750 cm$^{-1}$ (see the region delimited by the gray box in Figure 4.9) are due to interlayer interactions. As a matter of fact, the LO is the in-plane longitudinal mode, the ZO' is the interlayer breathing mode (in-phase interlayer vibration) and the ZO is the out-of-plane mode. From Figure 4.9 it is clear that the interlayer related features are observed only for the $^{12}\text{C}/^{13}\text{C}$ AB-BLG (red filled squares) and $^{12}\text{C}/^{12}\text{C}$ AB-BLG (blue filled circles). These observations are therefore a further signature of the presence of AB stacking. In addition, it is also clear that the region comprising frequencies from 1750 cm$^{-1}$ to 2050 cm$^{-1}$ are similar between the AB-BLG systems in contrast to the t-BLG and SLG. The spectral shape within these frequencies for AB-BLG systems could also be envisioned as another spectroscopic signature for confirming the existence of interlayer interactions.
Figure 4.9 Raman spectra of the combination modes in SLG and BLG systems from CVD-grown graphene. The spectral in the frequency range from 1650 to 1750 cm\(^{-1}\) (see the region delimited by the gray box) shows the combination of mode \(\text{LO}+\text{ZO}'\) and \(2\text{ZO}\), which are only observed in the two AB-BLG systems.

### 4.1.4 Percentage of AB-stacked bilayers

Furthermore, utilizing isotopically-labeled bilayers, we could rapidly verify the uniformity of the stacking orientation of our bilayer graphene over large areas. The asymmetry of the \(G'\) band is usually absent for CVD-grown \(^{12}\text{C}/^{12}\text{C}\) AB-BLG, while the FWHM of the \(G'\) band alone cannot uniquely distinguish between AB and turbostratic stacking. Besides TEM and SAED measurements are very time-consuming processes that are difficult to use for large-area samples. Therefore \(^{12}\text{C}/^{13}\text{C}\) BLG combined with Raman spectroscopy, as discussed in this chapter, allow us to identify the percentage of AB-
stacked regions more rapidly and accurately than other techniques. We found for our growth conditions discussed above, most of our bilayer graphene sample had AB-stacking; however, we also found some bilayer domains that showed regions with a mixture of AB stacking and turbostratic stacking, as shown in Figure 4.10, where we identify the AB-stacked regions by the FWHM of the G’ peak using a binary cutoff FWHM of 70 cm$^{-1}$. Other methods could also be used for differentiation between AB-BLG and T-BLG; however, we chose method for its simplicity. Figure 4.10 shows that many bilayer graphene domains are AB-stacked; however, we found that some bilayer graphene domains exhibited a mixed character (outlined with a red dotted line in Figure 4.10). From this 60 µm by 60 µm scan, we found that 79% of the bilayer flakes are pure AB-stacked, while the remaining bilayer flakes (21%) showed partial AB stacking (dominant) as well as some pure turbostratic stacking (rare). We attributed this to perhaps variations in the monolayer growth quality. Previous reports have shown that monolayer graphene nucleation could yield either single-crystalline or poly-crystalline flakes. The second layer of the bilayer flakes were assumed to be single crystalline due to their hexagonal symmetry; however, depending on the nucleation type of the first layer (single crystalline or poly-crystalline) and depending on whether the second layer grows across various domains, turbostratic regions within a bilayer flake are to be expected. This suggests that the fraction of AB-stacked versus turbostratic bilayer is also strongly coupled to the growth quality of the monolayer graphene.
Figure 4.10 Raman spectroscopy of bilayer graphene. (a) Raman mapping of integrated $G'$ FWHM of $^{12}\text{C}^{13}\text{C}$ BLG over an area of 60 $\mu$m by 60 $\mu$m. $^{12}\text{C}^{13}\text{C}$ AB-BLG (dotted white-line) and regions containing some $^{12}\text{C}^{13}\text{C}$ t-BLG (dotted red-line) are highlighted. (b) Representative Raman spectra taken from (a) are shown at corresponding positions, two t-BLG regions are shown (empty and filled squares) to indicate that these t-BLG regions have similar Raman spectra.

4.2 Identification of Growth Order

The location of the second graphene layer remains a controversial topic: at the time this investigation was carried out, one proposed growth mechanism suggests that the second layer is located on top; the other suggests that second layer grows underneath.\textsuperscript{173} For example, Kalbac \textit{et al.} reported on-top growth mechanisms by using hydrogen etching.\textsuperscript{174} On the other hand, Nie \textit{et al.} demonstrated that the second layer grows underneath on a flat Cu foil by carrying out low-energy electron microscopy (LEEM)/low-energy electron diffraction (LEED) measurement.\textsuperscript{113} This work has also initiated other studies: Li \textit{et al.} supported underlayer growth for graphene grown on the inside of
the Cu enclosure using isotope-labeling and time of flight secondary ion mass spectrometry (TOF-SIMS) mapping. Although there are different reports regarding whether the second layer grows on top or on the bottom (Figure 4.11), it is believed that the location of the second layer depends on the growth condition and on the technique used. Thus, establishing a fast and effective method for identifying and analyzing stacking order in bilayer graphene is highly desirable.

![Figure 4.11 Schematics of different bilayer graphene growth mechanisms. (a) On-top growth. The second layer grows on top of the first layer. (b) Underlayer growth. The second layer grows underneath the first layer. (c) Identifying the mechanism of the underlayer growth. The nucleation of the second layer occurs underneath the first grown monolayer. Then the bilayer continues to grow bigger below with the incoming carbon atoms diffusing from the edges of the monolayer.](image)

In our work, to determine the stacking sequence (whether the second layer grows on the top or below the monolayer), we used XeF$_2$ gas to fluorinate the exposed side of these hybrid isotopically-labeled bilayer graphene samples. Since the Raman spectra for the $^{12}$C and $^{13}$C layers were distinct and the second layer is largely composed of $^{13}$C, by selectively modifying the top surface we were able to identify whether the second layer grows on top or on the bottom. As reported by other groups, XeF$_2$ gas can be used to fluorinate graphene at ambient temperature, thereby creating a large amount of sp$^3$-bonded carbon which results in a drastic change in the Raman spectra. The combination of isotopic labeling and surface sensitive modification utilizing an oxygen plasma has recently been reported in identifying the stacking order of graphene grown on the inner surface of a copper envelope. In this thesis, we have developed the use of fluorination for stacking order differentiation due to the method’s lack of any directed plasma or focused energy that might damage either the upper and lower layers. We
conducted Raman spectroscopy after fluorination and compared the spectra from the same regions of the sample as shown in Figure 4.12. We found dramatic changes in the Raman spectra after fluorination: increasing D peak intensity, a broadening of the G peak, and a decrease of the G’ peak intensity due to doping and/or disorder effect. The D Raman peaks for $^{12}$C SLG and $^{13}$C SLG appear at 1340 cm$^{-1}$ and 1294 cm$^{-1}$, respectively. For the $^{12}$C/$^{13}$C BLG, even though the G peak for $^{12}$C graphene broadens, a small G peak for $^{13}$C graphene may still be observed at 1533 cm$^{-1}$ (indicated by an arrow), and the lineshape of this spectral feature is similar in shape to that of pristine $^{13}$C monolayer graphene. Moreover, a sharp G’ peak is observed at 2591 cm$^{-1}$ (indicated by an arrow), which further agrees with the presence of pristine $^{13}$C graphene. These observations indicate that the $^{13}$C layer deposited in the second step of the CVD process was not fluorinated, while only the $^{12}$C layer was fluorinated. This means that the $^{13}$C layer is on the bottom which was protected by the $^{12}$C layer located on top. After fluorination the turbostratic sample did not show a clear G’ peak for the $^{13}$C layer; however, the D peak (~1340 cm$^{-1}$) and G peak (~1603 cm$^{-1}$) both correspond to $^{12}$C and the absence of similar peaks corresponding to $^{13}$C still suggests that the $^{13}$C layer is underneath. Hence, we conclude that the second layer originated from below, between the substrate and the first layer, as shown in Figure 4.12. These results also agree with previous LEEM studies on Cu foils, Ru(0001), and Ir(111).$^{113,176,177}$ The second layer growing from underneath is currently understood to be due to carbon precipitation from the bulk or diffusion of carbon underneath the top layer. Mechanisms that have been proposed for growth from above suggest that graphitic fragments could be deposited from above, serving as nucleation sites; unfortunately, no stacking order is confirmed in this model.
Figure 4.12 Raman spectroscopy studies of fluorinated bilayer graphene to determine the growth mechanism for the second layer graphene. (a) Raman spectra of pristine $^{12}$C monolayer graphene (black), pristine $^{13}$C monolayer graphene (red), fluorinated $^{12}$C monolayer graphene (blue), fluorinated $^{13}$C monolayer graphene (turquoise), fluorinated $^{12}$C/$^{13}$C AB stacked bilayer graphene (magenta) and fluorinated $^{12}$C/$^{13}$C turbostratic bilayer graphene (gold). (b) Schematic of the top view of $^{12}$C/$^{13}$C bilayer graphene. (c) Schematic of the cross-section of $^{12}$C/$^{13}$C bilayer graphene during growth.

4.3 Bilayer Graphene Growth Mechanism

Here we investigate the growth mechanism by comparing the graphene films grown on both sides of the Cu enclosure for different lengths of time as shown in Figure 4.13. All the graphene layers were grown at 1045$^\circ$C under 1 sccm CH$_4$ and 50 sccm H$_2$. As mentioned in the chapter three, in this thesis, we transferred the graphene films onto SiO$_2$/Si substrates and present false colored optical images in order to highlight the
bilayer regions. The silicon dioxide is colored by white, while the different thicknesses of graphene are represented by different shades of pink.

Figure 4.13 Graphene growth on both sides of the Cu enclosure as a function of time. Here the graphene is transferred onto the SiO$_2$/Si substrate for better imaging. The different thicknesses of graphene are represented by different shades of pink. On the inside surface, after 60 min, there are some graphene monolayer flakes with a bi/tri-layer in the middle. When the growth time is 120 min, the graphene film growth is completed on the inside. The graphene growth process is divided into two stages according to the completeness of the monolayer growth on the outside surface of the Cu enclosure.

The bilayer graphene grown on the outside surface of the Cu enclosure can be divided into two separate stages by comparing the observed growth to that on a flat substrate. In Stage I, bilayers start to form in the middle of the monolayer flakes, while the monolayer, outlined by the white background, is not complete yet. Here both the flat Cu substrate and the enclosure show similar growth behaviors. However, in Stage II, even after the growth of the monolayer is completed, the bilayer graphene on the outside of the Cu enclosure continues to grow to a larger size, unlike the bilayer graphene on the flat foils which has stopped growing. Only at much longer times ($t > 90$ minutes) does the bilayer on the graphene eventually stop growing in size (Figure 4.14). This saturation time, interestingly enough, coincides very nicely with the growth of monolayer graphene on the inside. On the inside surface of the enclosure, there is no graphene formation for
the first 30 min. It takes much longer for the monolayer on the inside to coalesce into a complete film, and for this period of time, the bilayer on the outside surface continues to grow. Once the coverage of monolayer graphene on the inside surface is completed, the bilayer graphene on the outside surfaces also stops growing in size (Figure 4.14). Thus the fraction of exposed copper on the inside surface appears to affect the growth of bi- and tri-layer on the outside copper surface. This observation strongly suggests that the inside copper surface plays an important role for supplying additional carbon for the growth of the outside bilayer graphene.

Figure 4.14 Optical images of graphene transferred from the outside surface of Cu enclosure for a longer growth time (after the monolayer on the inside surface is complete). The growth condition is the same as that in Figure 4.13. After 2 hours, the coverage of bi/tri-layer graphene stops increasing, suggesting that the saturation of growth on the outside occurs once the inside surface is completely covered.

4.3.1 Pathway for Carbon Sources

Since the outside surface of the Cu enclosure is fully passivated within the first few minutes during the growth, the only catalytically active surface capable of providing active carbon is the inside surface of the enclosure. However, if this surface is responsible for the continued bilayer growth, how can the catalytic activity on the inside surface affect the bilayer graphene growth on the outside? To answer this question, we first examined two possible carbon diffusion pathways between the inside and outside surfaces of our enclosures: (1) gaps or holes when forming the enclosure edge, and (2)
the bulk copper itself. The SEM images at the crimped edges of a typical Cu enclosure (Figure 4.15 (a) and (c)) suggest that carbon can enter the inside of the enclosure through gaps at the edges. This is further confirmed by annealing the Cu enclosure at a higher temperature before growth to better weld the edges together, which resulted in almost no growth on the inside surface of the enclosure (Figure 4.15 (b) and (d)). Therefore, the graphene monolayer acts as a diffusion barrier, preventing any carbon from the outside from diffusing to the inside. As carbon leaks inside the enclosure, the carbon concentration builds up until a threshold concentration of carbon is reached that is necessary to nucleate graphene. However if carbon can leak in through these gaps, can carbon species also diffuse out and incorporate with the existing bilayer on the outside?

To address this possibility, we crimped a single piece of Cu foil to allow both a flat and an enclosed region to be created side by side (Figure 4.15 (e)). If the active carbon diffuses out through the gaps and goes underneath the monolayer graphene, it should attach to both the flat regions and the outside of the enclosure regions, enabling bilayers to grow on both surfaces. On the other hand, if the carbon diffuses through the Cu thickness, there should be a strong preference for bilayers to grow only on the enclosure. After growing for 1 hour, we can see that the bilayers are indeed much larger on the enclosure regions as compared to those on the flat regions. (4.15 (f)) As a result, we turn our attention to the second carbon diffusion pathway: diffusion through the bulk of the Cu foil.
Figure 4.15 Carbon delivery mechanisms. (a) Schematic of the Cu enclosure with gaps at the crimped edges, and a cross section SEM image on the right confirmed the presence of the gaps. (b) Schematic of the Cu enclosure with better sealed edges, with the corresponding SEM cross section image on the right. (c) Optical images of graphene grown on the inside surface of a Cu enclosure with additional annealing at 1065°C for 10 min at 420 mTorr. The Cu was first annealed in the shape of an enclosure at 1065°C. The enclosure was then opened after cooling down and, the copper was folded again into a new enclosure as usual (with a gap in between the edges). This result indicates that the annealing of the Cu foil does not affect the monolayer graphene growth on the inside surface. (d) No graphene grows on the inside surface when the annealing seals the enclosure at the edges. The growth condition is 1.5 sccm CH₄ and 50 sccm H₂ at 1050°C for 1 hour. (e) Illustration of a sample with both a flat region and an enclosure region where the sample was grown in parallel in the quartz tube. (f) Bilayer regions grow mostly on the enclosure region but not on the flat region.
To further verify the importance of the interior surface of the enclosure, we deposited $\text{Al}_2\text{O}_3$ via atomic layer deposition (ALD) (10nm thick, deposited at 125°C) as a passivation layer on one side of the Cu foil with the other side of the Cu foil coated with poly methyl methacrylate (PMMA) as a protection layer. After the deposition process, we removed the PMMA layer with acetone to expose the copper on that side and formed the Cu enclosure as usual with the ALD layer on the inside. Similar growth conditions were used (1 sccm CH$_4$ and 50 sccm H$_2$ at 1000°C for 2 hours). Under these growth conditions, the amorphous $\text{Al}_2\text{O}_3$ is transformed into crystalline $\text{Al}_2\text{O}_3$. There is no graphene grown on the passivated surface and the passivation layer is not detrimental to graphene growth on the non-passivated side. In Figure 4.16 (a), when there is no $\text{Al}_2\text{O}_3$ coating on the inside surface, the bilayer domains are large on the outside surface, consistent with the previous results in this thesis. In contrast, when there is a passivation layer on the inside surface of the Cu enclosure, the Cu enclosure fails to give large bilayer graphene on its outside surface (Figure 4.16).
If carbon sources actually diffuse through the Cu foil, the growth rate of bilayer graphene films should depend on the thickness of the Cu foil. To test this hypothesis, we utilized an etch mask constructed from Kapton tape in order to protect the outside surface, as well as to local regions on the inside surface. After electrochemical etching, the Kapton tape was removed and the calculated thickness of the Cu foil was computed by measuring the step heights using a Dektek Profilometer (Figure 4.17); after polishing, the roughness of the inside surface decreases. However, the properties of the outside surface of the Cu enclosure were preserved by capping the foil with Kapton tape during the polishing process.

![Graph showing etch rate over polishing time](image.png)

**Figure 4.17** Computed etch rate as a measure by Dektek Profilometer. We polished the Cu foil for 5 min, 30 min, 60 min and 120 min. The thicknesses of each type of the Cu foil were then measured to be 125 μm, 117 μm, 107 μm and 97 μm, respectively.
We folded the processed Cu foil with the trenched side facing inwards and grew graphene films following standard conditions (1.5 sccm CH₄ and 50 sccm H₂ at 1050°C) for 40 min. The graphene grown on the inside and outside were then transferred to silicon dioxide as shown in Figure 4.18 (c) and Figure 4.18 (d), respectively. The positions of the etched regions of the inside of the Cu enclosure are marked in Figure 4.18 (c) by a dotted line. It is interesting to note that the graphene growth on the inside surface has not been perturbed by the etching process and shows a relatively uniform nucleation density.

However, on the outside surface (Figure 4.18 (d)), at low optical magnifications, the transferred graphene from the regions of the thinned Cu foil appear to be optically more absorptive. By examining zoomed-in optical micrographs of these different regions (Figure 4.18 (e)), we indeed find that the bilayer graphene domain size is much larger on the thinner copper regions as compared to the unetched copper regions. Therefore, the shorter carbon diffusion time in the thinner Cu foil (etched regions) results in a larger amount of carbon at the outside surface available for the growth of bilayer graphene. This is also consistent with previous works that the bilayers grow from underneath the monolayer, as well as other recent work that has shown that carbon can diffuse through Cu thin films to the interface between copper and an insulating substrate to form graphene.⁸₄, ¹¹³, ¹₸¹, ¹₸²
Figure 4.18 Graphene growth on both surfaces of the Cu foil when the inside surface was patterned. (a) Illustration of the patterning process. The sample was covered on one side and patterned on the other side with the Kapton tape. After electro-chemically polishing, trenches were formed on only one side. Then the sample was folded with the patterns on the inside but the outside surface remained the same. (b) Surface profile of the
Cu foil surface as measured by surface profilometry (Dektek) (c) Optical images of the graphene grown on the inside surfaces of the Cu enclosures. The inside surfaces being etched are bounded by the dash lines. The inset in (c) and (d) shows a schematic of the copper enclosure. The highlighted side of the enclosure corresponds to which side of the copper has been transferred. (d), Comparison of graphene grown on the outside, corresponding to the patterns on the inside. (e) Higher magnification optical images of the graphene grown on the outside surface of the etched regions (orange border), the transition between etched and un-etched regions (blue border) and standard copper (red border).

To summarize, the investigations so far suggest that for the Cu enclosure, the inside environment is almost sealed so that CH$_4$ leaks into the Cu enclosure very slowly thereby delaying the Cu passivation on the inside surface. The exposed Cu surface on the inside serves as a catalytic pathway to continuously provide active carbon to the outside surface via carbon diffusion through the foil thickness. Potentially, atomic carbon radicals and/or CH$_x$ species could be diffusing through the Cu foil. This asymmetry between the growth rate of graphene on the inside and outside surfaces allows active carbon to diffuse through the Cu foil to grow bilayer graphene.

4.3.2 Growth Mechanism

From the above observations, we propose the following mechanism for the observed two-stage growth of bilayer graphene on the outside surface, as illustrated in Figure 4.19.

During stage I, the processes resemble that of flat copper samples where bilayer graphene growth is independent of the inside surface. The CH$_4$ gas adsorbs onto the Cu surface and decomposes to form active carbon species. Most of this active carbon leads to the formation of monolayer graphene while some diffuses underneath the monolayer graphene resulting in the formation of bilayer flakes. The final size of these bilayers is limited by the rapid growth rate of the monolayer film that serves as a diffusion barrier when grown to completion.$^{113}$ Furthermore, the fast completion of the monolayer
graphene growth on the outside also prevents carbon diffusion from the outside into the inside.

Stage II occurs after the outside monolayer graphene growth is complete. Based on our observations in Figure 4.19 (c), the inside surface shows no graphene formation for the first 30 min as carbon slowly leaks to the inside through the gaps. Similar to Stage I, CH$_4$ on the inside can decompose and form graphene on the inside surface. However, unlike Stage I, due to the slow growth rate of monolayer graphene on the inside, the free surface carbon can either readily diffuse through the Cu foil (to form bilayer graphene on the outside) or form graphene on the inside surface before it is fully covered with monolayer graphene. Thus, the large size of the bilayers on the outside is attributed to the carbon supplied during Stage II. As the coverage of monolayer graphene on the inside is almost completed, carbon diffusion through the Cu foil diminishes and the size of the bilayer graphene on the outside becomes saturated.
Figure 4.19 Explanation of the growth mechanisms. (a) The growth mechanism for bilayer graphene on the outside surface in stage I when the monolayer graphene is not complete yet. (b) The growth mechanism for bilayer graphene in stage II after the completion of the monolayer graphene at the outside surface. (c) The fitting of the experimental data to the model for the coverage of the exposed Cu on the inside and the bilayer graphene coverage on the outside vs time. (d) The diffusion process for carbon on the inside to go through the copper foil to form bilayer on the outside underneath the first-grown monolayer graphene.
4.3.3 Modeling

To better understand the growth mechanism, we modeled the kinetics of bilayer growth by simultaneously comparing the graphene growth rate on both inside and outside surfaces. Due to the coupling between the free catalyst area on the inside surface and the bilayer graphene growth on the outside surface, we first analyzed the graphene growth on the inside surface. In this analysis, we assumed that the growth of graphene on the inside surface is independent of the growth of graphene on the outside surface due to the rapid growth rate of the monolayer graphene on the outer surface which acts as a carbon diffusion barrier. It has been reported that the kinetics of the monolayer graphene growth on Cu using CH₄ can be represented using a modified Gompertz function. This model applies for graphene growth with the postulation that the graphene grows with a continual carbon input rather than by crystallization from a supersaturated solution. Therefore we employed this condition on the model for the monolayer graphene growth on the inside surface. The function \( p_{in}(t) \) is simplified to represent monolayer graphene coverage on the inside surface:

\[
p_{in}(t) = \frac{A_{in}(t)}{A_{tot}} = \exp\left\{ -\exp\left[ -R(t - t_0) + 1 \right] \right\}
\]

Eq. (4.2)

where \( p_{in}(t) \) is the fraction of monolayer graphene coverage on the inside surface of the Cu enclosure, \( A_{in}(t) \) is the area of the monolayer graphene coverage (\( \mu m^2 \)), and \( A_{tot} \) is the total area of the Cu inside surface (\( \mu m^2 \)). The value of \( R \) (\( \text{min}^{-1} \)) is determined by the maximum growth rate \( \mu_{max} \) (\( \mu m^2 \)) and the total copper area (\( A_{tot} \)); \( R = \frac{\mu_{max} e}{A_{tot}} \), where \( e \) is Euler's number. \( t_0 \) is the time lag (min), which is the time required for the concentration of the active carbon species to achieve a critical supersaturation level for the nucleation of graphene to take place. The formation of the active carbon species can occur both due to self-pyrolysis of the methane gas as well as by the assisted decomposition of the methane coming from the copper surface. Since the direct
thermal self-pyrolysis of the methane gas is energetically unfavorable, we focus on the catalytic role of copper, which helps decompose methane more effectively. There are a series of steps for the decomposition of CH\textsubscript{4} before the completion of the monolayer graphene growth on the inside surface. Nevertheless we simplified all the steps into one function, assuming that the governing rate-limiting constant \( k_d \) is determined by the slowest reaction step with the largest energy barrier \( E \): 

\[
[CH_4] \xrightarrow{k_d} [C*], \quad \text{where} \quad k_d = A \exp(-\frac{E}{kT}).
\]  

Eq. (4.3)

In equation (4.3), \([\text{CH}_4]\) and \([\text{C}*]\) (#/cm\textsuperscript{3}) are, respectively, the concentration of methane and active carbon species, while \( A \) is a pre-exponential factor, \( k \) is the Boltzmann constant and \( T \) is the temperature (K). This equation is valid assuming that there is sufficient methane gas inside the enclosure. The consumption of carbon diffusing through the Cu foil for bilayer growth should be much smaller than the input of carbon into the Cu enclosure, thereby ensuring that carbon inside the enclosure is never depleted. This assumption is supported by the fact that the monolayer graphene growth on the inside surface keeps increasing over time. Moreover, the concentration of methane is large enough so that the monolayer growth can be completed. However the reaction described above only occurs at regions with an exposed Cu surface. Therefore to calculate the effective carbon concentration on the inside surface, we need to only consider those regions not yet covered by graphene \( C_i(t) \) (#/cm\textsuperscript{3})

\[
C_i(t) = (1 - p_{in}(t))C*.
\]  

Eq. (4.4)

The carbon concentration gradient is developed throughout the Cu foil to drive the diffusion process (Figure 4.19 (d)). Here, \( C_i(t) \) (#/cm\textsuperscript{3}) is the carbon concentration on the inside surface, while \( C_2(t) \) (#/cm\textsuperscript{3}) is the carbon concentration on the outside. We assume that the carbon gets consumed immediately, once it arrives at the outer surface, implying that \( C_2(t) \) is zero. Another assumption is that we only consider the diffusion to be one-
dimensional (1-D) and there are no carbon sinks within the Cu foil. These assumptions lead to a concentration gradient that is a linear function of distance. Based on these assumptions, the flux of carbon diffusing through the Cu foil \( F_1(t) \) \((\text{#/s ptm}^2)\) is

\[
F_1(t) = D \frac{C_1(t)}{t_{cu}}. \quad \text{Eq. (4.5)}
\]

Here \( t_{cu} \) is the thickness of the Cu foil and the diffusion coefficient of carbon in the Cu foil is \( D \) \((\mu m^2/s)\). Assuming there is no loss of carbon during the diffusion process, we get

\[
F_1(t) = F_2(t) \quad \text{Eq. (4.6)}
\]

where \( F_2(t) \) \((\text{#/s·μm}^2)\) is the flux of carbon attaching to the bilayer graphene.

The growth rate of the bilayer on the outside is

\[
\frac{dA_{out}(t)}{dt} = F_2(t)A_{out}r, \quad \text{Eq. (4.7)}
\]

where \( r \) is the areal density, which is \(2.62 \text{ Å}^2/\text{atom}, \) which is obtained by

\[
6 \times \frac{\sqrt{3}}{4} \times (1.42 \text{ Å})^2 / 2 \text{ atoms}
\]

where \(1.42 \text{ Å} \) is the lattice constant of graphene.

Combining all the equations (4.2)-(4.7), we get

\[
\frac{dA_{out}(t)}{dt} = \frac{D}{t_{cu}} A \exp\left(-\frac{E}{kT}\right)C_{Cu}(1 - p_{in}(t))A_{out}r, \quad \text{Eq. (4.8)}
\]

where \( A_{out}(t) \) is the area of bilayer graphene \((\mu m^2)\) on the outside surface and \( r \) is the areal density of carbon atoms \((\mu m^2/\#). \) We rearrange equation (4.8) and at a given time \( t \) we write
\[ p_{\text{out}}(t) = \frac{A_{\text{out}}(t)}{A_{\text{in}}} = \alpha \int_0^t (1 - p_{\text{in}}(s)) \, ds , \quad \text{Eq. (4.9)} \]

where \( \alpha = \frac{D}{l_{\text{Cu}}} A \exp(-\frac{E}{kT} C_{\text{CH}_4} r) . \quad \text{Eq. (4.10)} \)

By plotting the equation (4.9) and fitting the experimental data to this simple model, we can get \( \alpha \) which is found to be equal to 1.61. According to equation (4.10), once the value of \( \alpha \) is obtained, we can link the experimental results with the modeling in Figure 4.19 and we can obtain a relationship between the diffusion coefficient of carbon (D) and the methane concentration inside the enclosure (\( C_{\text{CH}_4} \)).

In equation (4.10), there are two unknowns left to be determined. To estimate the diffusion coefficient of carbon in copper, \( D \), we need to estimate the methane concentration on the inside of the enclosure.

The methane gas supply is sufficiently large, because the leakage of methane into the Cu enclosure is more than the amount of carbon diffusing through the copper for bilayer growth. Therefore the growth rate of graphene can be expressed as follows:

\[ \text{rate} \propto C_{\text{CH}_4} \exp(-\frac{E}{kT}) \quad \text{Eq. (4.11)} \]

and this equation is then rewritten in the form:

\[ T \ln \left( \frac{\text{rate}}{C_{\text{CH}_4}} \right) \propto -\frac{E}{k} . \quad \text{Eq. (4.12)} \]

The highest monolayer growth rate is obtained from measuring the derivative of the coverage.
The growth rate of monolayer graphene is found to be 40.23%\%/min on the outside surface at 1000\(^\circ\)C, while it is 0.0261%\%/min (we extrapolated the fastest growth rate for both conditions) on the inside at 1050\(^\circ\)C. (Since monolayer graphene grows very quickly on the outside, it is easier to obtain the rate at 1000\(^\circ\)C instead of 1050\(^\circ\)C).\(^2\) Thus, by using equation (4.12), we get:

\[
1323 \ln \left( \frac{0.0261}{C_{\text{inside}}} \right) = 1273 \ln \left( \frac{40.23}{C_{\text{outside}}} \right)
\]

Eq. (4.13)

The methane concentration on the outside can then be estimated:

\[
C_{\text{outside}} = \frac{n}{V} = \frac{P}{RT} = \frac{1.7 \text{Tor} \times 133 \text{Pa/Tor} \times 1}{8.31 \text{J/(Kmol)} \times 1323 \text{K} \times 50} = 4 \times 10^{-4} \text{mol/m}^3
\]

Eq. (4.14)

where 1/50 is the fraction of methane to argon used in our growth conditions.

By plugging in the value of \(C_{\text{outside}}\), we obtain \(C_{\text{inside}}\) is \(4 \times 10^{-7} \text{mol/m}^3\).

Thus we find that the methane concentration on the inside is approximately 1000 times less than that on the outside computed at the peak growth rate. While we have assumed a constant carbon concentration as a function of time, in reality the inside carbon concentration will change as a function of time as more and more methane leaks inside the enclosure; however, due to the slow diffusion of methane to the inside pocket (based on the relatively linear growth rate of monolayer graphene on the inside at the beginning) we choose for simplicity to assume a constant carbon concentration.

After obtaining the CH\(_4\) concentration, we go back to what we got from equation (4.9)

\[
\frac{D}{t_{\text{Cu}}} A \exp(\frac{-E}{kT}) C_{\text{CH}_4} r = \alpha,
\]

Eq. (4.15)
the value of $\alpha=1.61$ is obtained by fitting the experimental data to the plotting.

Using $t_{Cu}=127\mu m$ as the thickness of the Cu foil (ignoring the copper loss during the Ni etchant cleaning and annealing processes) and

the pre-exponential factor $A=2.8\times10^{16}$ s$^{-13}$, 

the energy barrier for methane decomposition $E=1.7eV$, 

and the areal density of carbon atoms $r=2.62 \frac{4^2}{\#}$, which is obtained by

$$6 \times \frac{\sqrt{3}}{4} \times (1.42 \AA)^2 \div 2 \text{atoms},$$

the methane concentration on the inside $C_{CH_4}=4\times10^{-7}$ mol/m$^3 \times N_A=2.4\times10^{17}$,

By plugging all the numbers into equation (4.15), we get $D$ is $3.36\times10^{-12}$ m$^2$/s.

In summary, by extracting the fitting coefficient and by estimating the concentration of methane on the inside surface, we estimate the diffusion coefficient of carbon passing through the copper to be $3.36\times10^{-12}$ m$^2$/s, which is an order of magnitude less than the diffusion coefficient of carbon in metals with a higher carbon solubility, such as iron ($3.6\times10^{-11}$ m$^2$/s at 1050°C). Therefore the diffusion coefficient of carbon through the copper microstructure is non-negligible, thereby supporting our assumption that carbon can diffuse through the Cu foil. Other recent work that has also shown that carbon can diffuse through Cu thin films to the interface between Cu and an insulating substrate to form graphene.
4.3.4 Coverage dependence on the thickness of the Cu foil

To verify our model (Eq. 4.8), we also grew bilayer graphene with various thicknesses of Cu foil ($t_{\text{Cu}}$). To utilize the same purity and type of Cu foil throughout the experiment, we purposely varied the thickness of our Cu foil by electrochemically polishing our Cu foil in dilute phosphoric acid. After growth under 1.5 sccm CH$_4$ and 50 sccm H$_2$ at 1050$^\circ$C for 1 hour, the coverage of the bilayers (dotted blue), trilayers (dotted red), and all the carbon content (black) on the outside were plotted as a function of $1/t_{\text{Cu}}$ in Figure 4.20. The blue line shows that the bilayer coverage saturates around a $t_{\text{Cu}}$ of 107 $\mu$m; however, Eq. 4.8 predicts a linear relationship between the bilayer coverage and $1/t_{\text{Cu}}$. To explain for this discrepancy, in most of our previous growth conditions, the inside monolayer graphene coverage was completed before the trilayer coverage has become appreciable; therefore we have assumed that the integrated carbon content mainly contributes to the bilayer coverage. However, for thinner foils, the carbon delivery rate is much faster than before, such that, the trilayer graphene is able to grow before the inside graphene fully passivates the copper surface. In Figure 4.20 (c), when the Cu foil was thinned down to 57 $\mu$m, the optical image shows that the trilayer graphene become almost continuous and even quadlayer graphene starts to appear. However, the percentage of quadlayer coverage is only about four percent.
Figure 4.20 The graphene grown on Cu foil with different thicknesses. (a) The coverage of bilayers (dotted blue), trilayers (dotted red) and the summation of both bilayers and trilayers (dotted black) as a function of thickness of the Cu foil. The linear fitting of the carbon content is shown in solid black line. (b) Transmittance of the layer-by-layer transferred graphene films (black) and directly grown graphene films on the Cu enclosures with thickness of 107 μm (red) and 57 μm (blue), respectively. The inset shows the photograph of the corresponding graphene films on the borosilicate. The layer-by-layer transferred graphene was used as a reference and the transmittance measured at
550 nm was 97.7\%, 95.35\%, and 92.96\% with increasing numbers of layers. The transmittance for the LPCVD grown graphene films at 550 nm was 95.7\% (107 \mu m) and 93.97\% (57 \mu m). (c) Optical images of the graphene films grown on the outside of the Cu enclosure with different thicknesses.

Our simple model only looks at the total carbon content delivered to the outside surface. Therefore, we plot the total integrated carbon content (black) by summing up the percent coverage of both the trilayer and bilayer graphene. Additionally, based on Eq. 4.7, by fitting the coverage vs. thickness plot, we calculated the diffusion coefficient to be $3.16 \times 10^{-12}$ m$^2$/s with a goodness of fit ($R^2$ equals to 0.98). This value is consistent with our previously extracted value $3.36 \times 10^{-12}$ m$^2$/s, which we obtained through modeling the time dependent growth of our bilayer graphene on the outside. In Figure 4.20 (b), the transmittance of graphene film grown on the Cu enclosure was measured and compared with reference samples of layer-by-layer transferred graphene films. For the reference samples, the transmittance measured at 550 nm was 97.7\%, 95.35\%, and 92.96\% for 1L, 2L, and 3L of graphene, respectively. Each graphene layer absorbs $2.3 \pm 0.1\%$ of the incident light at 550 nm, consistent with other reports from literature.$^{26}$ For graphene grown on the Cu foil with a thickness of 107 \mu m, the calculated transmittance given the computed coverage from Figure 4.20 (1L = 100\%, 2L = 94\%±2\%, 3L = 6\%±1.5\%) is 95.7\%. Additionally, for the graphene films grown on a 57 \mu m thick Cu foil (1L = 100\%, 2L = 100\%, 3L = 72\%±11\%), the total calculated optical transmittance is 93.97\%. The small discrepancy (+0.35\% for 107 \mu m and +0.23\% for 57 \mu m) for both films suggests that the film is slightly more transparent than calculated. We attribute this small discrepancy to possible non-uniformities across the film as well as non-uniformities introduced during the transfer processes, such as rips or tears.
4.3.5 Two-stage Growth

By applying our understanding of the growth mechanism to interpreting our experimental results, we can utilize a two-step growth process for controlling the nucleation and the carbon delivery for bilayer graphene following similar work done for growing larger domain monolayer graphene. Based on the origin of the carbon source, the growth process is divided into two stages: in Stage I, bilayers nucleate and start to grow due to the carbon provided from the outside; in Stage II, bilayers continue to grow by using the carbon provided from the inside surface of the Cu enclosure. There are two growth conditions that we used; we denote the low methane flow condition (1 sccm) as “Condition 1”, and the high methane flow condition (5 sccm) as “Condition 2”. To obtain a more complete picture, we consider all four scenarios possible with these two conditions applied to the two growth stages; the results are shown in Figure 4.21. It has been reported that the low methane flow rate results in a low nucleation density and therefore a larger domain size. In the case of our two-stage growth, the nucleation of bilayers takes place in Stage I. Thus, in order to maximize the bilayer domain size, we choose Condition 1 for Stage I. Given the fixed conditions in Stage I, we can tune the coverage of the bilayers by varying the methane flow rate in Stage II. We note that using a low methane flow rate in Stage II results in a lower bilayer coverage but also results in more multilayer regions (Figure 4.21 (a')), while a higher flow rate results in a more uniform bilayer coverage (Figure 4.21 (b')). Therefore, in order to obtain large-domain high-coverage bilayer films, in addition to using a low methane flow rate for Stage I to obtain a lower nucleation density, we use a higher methane flow rate during Stage II to achieve uniform high coverage bilayers (Figure 4.21 (b')).
In this section, we present a follow-up work utilizing the carbon diffusion process through Cu enclosures. In the previous work, we proposed that the diffusion of carbon is driven by the concentration gradient across the Cu foil. Therefore, here we reversed the direction of the carbon diffusion by placing a carbon sink (W foil) on the inside of the enclosure, and we found that bi-/multi-layers can be selectively removed from the outside surface so that a more uniform monolayer graphene can then be obtained. We observe
that the bi-/multi-layers graphene that nucleate underneath monolayer graphene can be selectively removed as the growth time is increased. Both X-ray photoelectron spectroscopy and X-ray diffraction reveal the formation of tungsten sub-carbide (W₂C), suggesting the role of the W foil as a carbon sink, that alters the carbon concentration inside of the enclosure. (Figure 4.22) Consequently, the bi-/multi-layers appear to dissolve away. Finally, utilizing this selective removal process, we are able to demonstrate large-domain (> 200 µm) monolayer graphene that is free of any bi-/multi-layers by using Cu double enclosures. The formation of large-area single-domain monolayer graphene can enable large-scale integration of graphene devices into the applicating world with high yield and high reproducibility.

High-quality large-area graphene synthesis has already been demonstrated using the CVD method. ⁹⁰, ⁹⁶, ¹¹⁹, ¹⁹¹ In particular, large-domain graphene (>100 µm) has been achieved with a quality comparable to that of exfoliated graphene using a Cu enclosure. ¹¹², ¹⁷² This approach has enabled the synthesis of graphene under low CH₄ conditions to achieve extremely low nucleation densities.¹⁷² Unfortunately, while reducing the carbon flow significantly, the enclosure method often results in the formation of bi-/multi-layers in the film. ¹³⁸, ¹⁷² Under these low growth rate conditions, there are more surface edges available in the monolayer graphene for the diffusion of carbon underneath the monolayer to form bi-/multi-layers. ⁸⁴, ¹¹³ As a consequence, large monolayer domains and large bi-/multi-layer domains (20 µm-100 µm) have been found to appear hand-in-hand. However, the different electronic properties of bi-/multi-layers can reduce the homogeneity and transport of electronic carriers within the monolayer graphene. ⁷, ⁴⁷ To achieve uniform monolayer graphene, various methods have been explored, such as tuning growth conditions ¹³⁸, ¹⁹² and pretreating the Cu using etchant cleaning, electro-chemically polishing, and many-hour annealing ¹⁴⁰, ¹⁴¹, ¹⁹³. Nevertheless, bi-/multi-layers can still be observed very often. ¹¹⁸, ¹³⁸, ¹⁸⁴, ¹⁹², ¹⁹⁴.
On the other hand, we can suppress the size of the bilayers of graphene through a faster growth rate of monolayer graphene by applying a higher CH₄ concentration, but the monolayer domain size will then be compromised. As a result, techniques to circumvent the competition between optimizing monolayer domain size and optimizing layer uniformity are required.

### 4.4.1 Growth of Uniform Monolayer Graphene using Cu Enclosures

Our previous work has shown that by using Cu enclosures for graphene synthesis, a high coverage of bilayer graphene can be achieved on the outside surface of the enclosure because carbon species on the inside can also diffuse out from the enclosure to form bilayers on the outside. The carbon diffusion process is driven by the concentration gradient across the Cu foil. Here, we reverse the direction of the carbon diffusion by placing a carbon sink (W foil) on the inside of the enclosure, and we have found that bi-/multi-layers can be selectively removed from the outside surface so that uniform monolayer graphene is then obtained on the outside of the Cu enclosures.

Figure 4.22 shows the optical images of the transferred graphene films (on SiO₂/Si substrates) grown on a flat Cu foil, an empty Cu enclosure, and a Cu enclosure with a tungsten (W) foil inside (illustrations shown in the insets of Figure 4.22). Small bilayers can be observed on the flat Cu foil (Figure 4.22 (a)), due to the diffusion of carbon atoms underneath the first grown monolayer at the nucleation stage. On the other hand, monolayer graphene with high-coverage bi-/multi-layers appears on the outside of the empty Cu enclosure in Figure 4.22 (b), which is consistent with our previous report. For a typical graphene growth on a Cu enclosure, the carbon can leak slowly into the inside of the enclosure through the gaps at the edges, forming a carbon source on the inside, which can diffuse out to form bi-/multi-layers. However, for Cu enclosures with a piece of W foil enclosed, there is no graphene growth on the inside of the enclosure. This observation suggests that the carbon supply to the monolayer graphene is significantly
reduced by the presence of the W foil. In addition, it has been reported that the presence of the W foil does not interfere with the growth of graphene on Cu\(^{105}\), nor does W inter-diffuse into Cu\(^{105}\). At the same time, the graphene on the outside surface is uniform with no bi-/multi-layers present in Figure 4.22 (c). This indicates that there is no available carbon source provided from the inside of the enclosure, in agreement with the observation that no graphene forms on the inside.

Figure 4.22 Optical images of graphene grown on: (a) a flat Cu foil, (b) the outside surface of the Cu enclosure and (c) the outside surface of the Cu enclosure with a W foil inside. See insets on upper right hand corner of (a), (b) and (c). The different thicknesses of graphene are represented by different shades of pink. The darker regions are bilayers or multilayers graphene.

To investigate the growth mechanism of uniform monolayer graphene, we compare in Figure 4.23 the graphene films grown on the outside of the Cu enclosures with and without W enclosed for different lengths of time. For the first 10 min, bi-/multi-layers indeed nucleate in the center of the monolayer graphene flakes on both of the Cu enclosures.\(^{80}\) As time progresses, for the empty Cu enclosure, the monolayer becomes complete and the bi-/multi-layers continue to grow larger due to the continual flow of carbon from the inside of the enclosure. In contrast, for the Cu enclosure with the W foil, the bi-/multi-layers start to diminish in size and eventually disappear after one hour.
Figure 4.23 Optical images of transferred graphene grown on the outside of the Cu enclosure as a function of time. On the outside surface of the Cu enclosure, the bilayer on the outside continues to grow. In contrast, bilayers grow during the first 20 minutes but start to disappear on the Cu enclosure where the W foil is inside the Cu enclosure. The monolayer graphene film remains uniform for the rest of the growth time of up to 2 hours.

Additionally, high resolution SEM images also confirmed that the graphene grown on the Cu enclosure (when the W foil is contained inside the Cu enclosure) is uniform monolayer with no bi-/multi-layers. At the same time, no graphene grows on the inside, indicating that the concentration of carbon sources is extremely low. However, when we grow graphene under the same conditions for five hours, bi-/multi-layers start to appear again on the outside and graphene grows on the inside simultaneously.

Figure 4.24 High resolution SEM image of graphene grown on Cu with and without a W foil enclosed. (a) The monolayer graphene is uniform with no bi-/multi-layers on the outside of the Cu enclosure with a W foil enclosed. (b) Small bilayer flakes are seen simultaneously on the flat Cu foil.
On the basis of the above discussion, we prepared graphene films using an empty Cu enclosure and a Cu enclosure with a W foil enclosed, respectively. (Figure 4.25) After transferring graphene film onto SiO$_2$ substrate, we performed XPS and Raman spectroscopy on both samples. In Figure 4.25, XPS survey results (black) shows that there is no W signal on the graphene grown on the empty Cu enclosure, indicating no W contamination in the growth system. However, for graphene grown on the Cu enclosure with the W foil, the XPS results (red) are the same as the reference sample, which indicates that there is no W impurity even with the W foil enclosed throughout the growth process. (Figure 4.25 (a)) The reason that there is no W on the graphene is probably because the melting temperature of W is very high (~3422°C). Meanwhile the growth temperature (1045°C) is close to the melting temperature of Cu (~1,085°C), so that Cu can easily get evaporated and coated onto W but not vice versa. (Figure 4.25 (b)) Furthermore, the Raman spectra from both samples confirmed that the graphene grown on the Cu enclosure with the W enclosed is the same as the reference samples. There is no discernible D band in both Raman spectra, suggesting the growth of a high quality graphene film. Both the G bands are located at 1587 cm$^{-1}$ while the 2D bands are located at 2674 cm$^{-1}$, (black) and 2675 cm$^{-1}$(red), indicating a similar doping level for the two cases. Thus, we conclude that there are no W impurities that caused any defects or extra doping in the graphene films.
Figure 4.25 Comparison of graphene grown on a Cu enclosure with and without W foil. (a) XPS survey on transferred graphene on SiO	extsubscript{2} substrate. (b) High resolution XPS near the C\textsubscript{1s} peaks for calibration but now including for W4d\textsubscript{5}/W4d\textsubscript{3} and C\textsubscript{1s} peaks. (c) Raman spectra from the same transferred samples.

4.4.2 Isotopic Labeling During Growth Process

Since the bi-/multi-layers grow at the beginning and then disappear later, a question arises: is the monolayer graphene also affected by the W? To answer this question, we utilize \textsuperscript{12}C and \textsuperscript{13}C carbon isotopes (\textsuperscript{13}CH\textsubscript{4} and \textsuperscript{12}CH\textsubscript{4}) to identify the carbon incorporation as a function of time. We grew graphene by sequentially flowing \textsuperscript{13}CH\textsubscript{4} for the first 15 min and then \textsuperscript{12}CH\textsubscript{4} for the remaining time using a Cu enclosure with W foil inside. Based on the time dependent studies in our previous work, we expected that the monolayer and bi-/multi-layers on the outside surface should be solely composed of
If the graphene is being substituted during the growth process by the incoming carbon, $^{12}C$ will be incorporated into the films. Finally, using Raman spectroscopy, we can locate and differentiate the various carbon isotopes. The positions of the Raman peaks are dependent on the masses of $^{12}C$ and $^{13}C$. We thus performed Raman mapping on the graphene grown on the outside surface of the Cu enclosures with a W foil enclosed. The G peak position of the monolayer composed of $^{12}C$ and $^{13}C$ is located at around 1583 cm$^{-1}$ and 1535 cm$^{-1}$, respectively. The percentages of $^{12}C$ and $^{13}C$ were extracted and plotted in Figure 4.26 and Figure 4.27. The absence of $^{12}C$ throughout the entire process suggests that the film is completely composed of $^{13}C$, implying that under the same growth condition, no substitution of carbon in the monolayer occurs. Only the small bilayer regions grown at the beginning disappear, while the monolayer regions remain intact. This observation is also supported by previous reports that once Cu is fully covered, there is no catalytic surface to further decompose $^{12}CH_4$. The difference in the results of the monolayer and small bi-/multi-layers is probably due to the edges of graphene. It is possible that the edges of the small bilayers are unbounded and chemically active. With the assistance of the catalytic Cu foil, the reaction of graphene formation is reversed, such that graphene is etched back to carbon, diffuses inwards through the Cu foil, and is eventually consumed by the W foil. In contrast, the edges of monolayer graphene domains are bonded to adjacent grains, thereby making them more stable as compared to that of the bi-/multi-layers.
Figure 4.26 Statistics of G peak position for graphene grown on the outside of the Cu enclosures with W enclosed. Graphene was prepared by introducing $^{13}\text{CH}_4$ for the first 15 min, then switched to $^{12}\text{CH}_4$ for a total growth time of (a) 30 min, (b) 1 hour, (c) 2 hour and (d) 5 hours.

Figure 4.27 Percentage of the 12C and 13C isotope in monolayer graphene grown using isotopic labeling.
4.4.3 XPS and XRD Studies

To elucidate the role of the W foil, we use a combination of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to study the change of the chemical composition of the W foil. We performed XPS on both the outside and inside surfaces of the Cu enclosure and found that there is no presence of W. On the other hand, there is a presence of Cu on the W foil after 1 hour of growth, as shown in the inset in Figure 4.28 (a). This is expected because the growth process was carried out at 1045°C, which is close to the melting temperature of Cu, resulting in Cu evaporation on the W foil during the growth process. To show that the thin Cu layer on W does not affect the role of the W, we put a W foil into a Cu enclosure for annealing under 10 sccm H₂ at 1045°C for 1 hour. Then, we removed the W foil which had been coated with a thin layer of Cu and repeated our previous growth utilizing a Cu-coated W foil in place of our standard W foil. For the same growth condition, we found that uniform monolayer graphene can still be obtained.. Figure 4.28 (b) shows the XRD results on as-received W (without any growth), W after one hour growth (inside the Cu enclosure), W after five hours growth and as-received WC, respectively.

In Figure 4.28 (b), for W after five-hour growth, the W₂C peaks are evident, as highlighted by red asterisks. Formation of WC was reported by annealing graphene oxide and tungsten oxide, however, here we found that W₂C forms on the W under our growth conditions. Moreover, recent research has shown that W₂C is stable even at high temperature and with more carbon source provided. The formation of W₂C indicates that the carbon source is slowly being incorporated into the W. Nevertheless, the W₂C peak is not observed after only one-hour growth. This can be explained by the fact that there are no significant amounts of detectable W₂C present due to the low carbon concentration on the inside at the beginning of the growth process. In Figure 4.28 (c), high resolution XPS of C1s confirms the presence of W₂C, located at 283.6 eV, which
can be distinguished from WC at 282.6eV. All the peaks are fitted with Gaussian functions of different widths. The peak located at around 284.6eV with full width half maximum (FWHM) larger than 1eV is from the presence of adventitious carbon adsorbed on the surface, instead of graphene or graphite formation. For graphene or graphite, the FWHM of the peak is much narrower (< 1eV).
Figure 4.28 Characterization of the graphene grown on Cu enclosures with W and the composition analysis of the W foil. (a) XPS results on W and on both inside and outside surfaces of the Cu enclosures. (b) XRD results on as-received W foil (black), W foil after
1-hour (blue) and 5-hour growth (red), and as-received WC (grey). (c) Detailed XPS spectrum of C1s. Fitted peaks are shown with dashed lines.

### 4.4.4 Cu Double Enclosure

Since the W foil removes the bilayer graphene from the outer surface of an enclosure, we can utilize this method for preparing large-domain bi-/multi-layers-free graphene using a Cu double enclosure geometry. The schematics of the Cu double enclosure are shown in Figure 4.29. The W foil is placed inside the small Cu enclosure, which itself is placed inside a larger Cu enclosure. The surfaces on both sides of the Cu enclosures are numbered from the inside to the outside. For example, the innermost surface of the small enclosure is labeled surface 1 and the outside surface of the big enclosure is labeled surface 4. After growth under the same conditions for different lengths of time, graphene films on surface 2 and 3 were transferred and compared. After 1.5 hours, the domain size of graphene is more than 200 µm. In the center of the domains, we can find bi-/multi-layers. As time proceeds, the monolayer graphene growth is complete and bi-/multi-layers graphene continue to grow larger on surface 3 (highlighted in red). In contrast, the bi-/multi-layers on surface 2 start to disappear, resulting in a uniform monolayer. Both surface 2 and 3 are exposed to the same environment with the same gas composition and temperature. However, because of the presence of a W foil inside the small Cu enclosure, the bi-/multi-layers underneath surface 2 can be removed, consistent with earlier observations on the outside of one Cu enclosure. However, the bi-/multi-layers on surfaces 3 and 4 remain because both surfaces of the Cu enclosure are fully covered by graphene monolayers, which act as a carbon diffusion barrier.113
Figure 4.29 Optical images of graphene grown on Cu double enclosures. (a) Schematics of the Cu double enclosures. (b) Growth mechanism for bi-/multi-layer graphene on surface 2 disappears while growth remains on surface 3. (c) Comparison of graphene grown on the surface 2 and 3 as a function of time.

In order to probe the domain size of the graphene, we carried out further characterization using TEM. We recorded the diffraction patterns at different locations of the sample. There were no discontinuous changes in the orientation of the diffraction spots, indicating that there were no rotational domain boundaries. Results in Figure 4.30 showed that the diffraction patterns were the same at different locations, suggesting that the monolayer on surface 2 is composed of a large single graphene domain over 200 μm in size.
Figure 4.30 Large single domain monolayer graphene. The hexagonal diffraction patterns were taken from the corresponding locations on the graphene domain in the SEM image in the center, showing 6 similar diffraction patterns.

In summary, uniform bi-/multi-layers-free monolayer graphene is obtained using Cu enclosures with a W foil enclosed inside the innermost Cu enclosure. During the growth, the bi-/multi-layers underneath the monolayer graphene are selectively removed while the monolayer remains intact. The W foil plays an important role in maintaining a low carbon content inside of the Cu enclosure by itself absorbing carbon. Both XRD and XPS results indicate the formation of W$_2$C on the W foil. Finally, using double Cu enclosures, we were able to achieve uniform large-domain graphene with no bi-/multi-layers. The formation of large-area single-domain monolayer graphene can enable large-scale integration of graphene devices with high yield and high reproducibility.
Chapter 5: Synthesis of Hexagonal Boron Nitride

Chapter 5 discusses the synthesis and characterization of thick multilayer hBN using Fe foils, and monolayer to a few layer hBN using Pt foils. First, we will review the previous results from former group members. Then we will discuss the improvement on the synthesis of hBN and the investigations on the effects of the growth conditions on the thickness of the resulting hBN film, such as the flow rate and the growth time. Higher flow rate and longer growth time can increase the thickness of hBN. Moreover, we carried out characterization of the obtained hBN films by Raman spectroscopy, TEM and optical absorption. During the growth, we also found that the growth of hBN is highly dependent on the underlying crystal orientation of the Fe foil; hBN prefers to nucleate first on specific Fe orientations. Additionally, the triangular hBN as well as hBN ribbons can be found on different Fe grains. In the second part, we discuss the growth and characterization of monolayer hBN on Pt foil. We found thick hBN can also be prepared using Pt foil and the characterization is discussed as well.
5.1 Hexagonal Boron Nitride using Fe Foils

5.1.1 Previous Development on the Synthesis of Thick Multilayer hBN using Fe Foils

In this section, previous works that have been developed by former group members - Dr. Kikang Kim, Dr. Soomin Kim and Dr. Allen Hsu - are presented. They were able to successfully prepare thick multilayer hBN using Fe foils and performed characterization to prove that the hBN can serve as the substrate for graphene to enhance the mobility of graphene FETs. The improvement on the growth conditions and further characterizations will be discussed in section 5.1.2.

Figure 5.1 (a) and (b) show the optical images of a transferred hBN film on a SiO$_2$/Si substrate. The film is continuous and covers a 3 cm by 3 cm region. However, the thickness in the hBN film is not uniform; the brighter regions in Figure 5.1 (b) represent thicker hBN films. Figure 5.1 (c) shows the corresponding Raman mapping of Figure 5.1 (b). The intensities of the E$_{2g}$ peak varies across the films, indicating that the numbers of layers are different in various locations. Figure 5.1 (d) shows the Raman spectra taken from three different locations in Figure 5.1 (c). The peaks located at ~ 1366 cm$^{-1}$, which is a characteristic peak of hBN. However, it is hard to differentiate the number of layers from the Raman peaks.
Figure 5.1 Characterizations of transferred hBN films. (a) and (b) Optical images of a transferred thick hBN film on a SiO₂/Si substrate. (c) Corresponding Raman mapping of (b). (d) Raman spectra taken from (c).

Figure 5.2 (a) shows the AFM images of the CVD-grown hBN film. A scratched region was intentionally created for the measurement of the thickness of the thick hBN regions. In contrast to graphene, when the hBN films get thicker (more than 4 layers), it is hard to differentiate the number of layers. Therefore, measuring the height profile across the hBN substrate steps was found to be more effective. In Figure 5.2 (b), the profile shows us that the hBN film is about 15 nm thick, which is ideal for being used as the substrate to smooth out the roughness from the underlying SiO₂/Si substrate.
Figure 5.2 Measurement of the thickness of the hBN film on SiO$_2$/Si substrate after the transfer process. (a) AFM image of scratched region for the estimation of h-BN thickness. (b) Height profile along the solid line in (a). The profile of the cross section measurement shows that the hBN is ~15 nm thick.²⁰⁸

Moreover, Dr. Allen Hsu performed characterizations on the electrical properties of thick multilayer hBN. Figure 5.3 (a) shows a schematics of a device using CVD-grown hBN as the substrate and with CVD-grown single-crystal graphene on top. The inset of Figure 5.3 (a) shows an optical image of an actual device. The conductance ($\sigma$) of graphene as a function of applied back gate voltage ($V_{BG}$) is plotted in Figure 5.3 (b). The red curve represents the CVD-grown graphene on a CVD-grown multilayer hBN film while the black curve represents the CVD-grown graphene directly on the SiO$_2$/Si substrate. Comparing the Dirac points of the two curves, the Dirac point of the red curve is closer to 0V, indicating less doping in the graphene on hBN films. Moreover, the slope of the red curve is steeper, suggesting that the hole and electron mobility ($\mu_p$ and $\mu_n$) are higher. Figure 5.3 (c) summarized all the results on the intrinsic doping level ($n_{\text{dirac}}$) and the hole mobility ($\mu_p$). Although the results for graphene on hBN are more scattered, we found that the carrier mobility of some devices on hBN exceed 10,000 cm$^2$V$^{-1}$s$^{-1}$, which is comparable to the results for graphene devices on exfoliated hBN.² Dr. Hsu suggested that the variation in the performance of graphene devices are attributed to the large
bubbles and non-homogeneity during the transfer process. Figure 5.6 (d) and 5.6 (e) show graphene devices with carrier mobilities of \( >10000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) and \( < 2500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), respectively. Indeed, there are more wrinkles and bubbles present in graphene devices in Figure 5.3 (e).

![Graphene devices with carrier mobilities](image)

Figure 5.3 Electrical properties of multi-layer h-BN and graphene on an hBN substrate. (a) Schematic diagram of a graphene FET on h-BN. The inset shows the optical image of a real device. (b) The representative conductance (\( \sigma \)) of the graphene channel as a function of applied back gate (\( V_{BG} \)) at room temperature with a \( V_{DS} = 100 \text{ mV} \) on \( \text{SiO}_2 \) (blue) and on h-BN/\( \text{SiO}_2 \) (red) substrates. (c) The plot of the extracted hole mobility (\( \mu_p \)) versus \( n_{\text{Dirac}} \) for both of the substrates (h-BN and \( \text{SiO}_2 \)). AFM images of a (d) high carrier mobility (>10000 cm²V⁻¹s⁻¹) and (e) low carrier mobility (<2500 cm²V⁻¹s⁻¹) device. The wrinkles and air bubbles of graphene or hBN are seen, resulting in different conductance of devices.²⁰⁸

### 5.1.2 Synthesis and Characterization of hBN grown on Fe foils

From this section, we will present the follow-up work on the synthesis of thick multilayer hBN. We found that the thickness of hBN is dependent on the growth
conditions such as the growth time and the flow rate. Figure 5.4 shows the SEM images of different morphologies of hBN on Fe substrates using different growth conditions. In Figure 5.4 (a), discrete triangular monolayer hBN flakes were obtained by flowing for 1 hour 0.1 sccm H₂ as the carrier gas and 100 sccm H₂ for dilution. For some monolayer flakes, much thicker film are found near the center, suggesting that the thick films grow at the beginning of the growth process. Also, the while lines across the flakes are wrinkles resulting from the negative thermal expansion coefficient of hBN, which causes the hBN film to expand upon cooling. Further extension of the growth time to 1.5 hour using the same flow rate (0.1 sccm H₂ carrier gas and 100 H₂) is expected to lead to a continuous film as well as some thick regions, as shown in Figure 5.4 (b). For comparison of the flow rate, we keep the same growth time and adjusted the flow rate of the carrier H₂ gas from 0.1 to 0.2 sccm. With the increase of the precursor dose, the hBN formed a complete film with much thicker hBN films in triangular shapes. These results suggest that different growth conditions could be used for specific needs. Nevertheless, further optimization of the synthesis process of hBN growth is needed to improve the uniformity of the hBN film.

Figure 5.4 SEM images of hBN on Fe with different growth conditions. (a) 0.1 sccm H₂ as the carrier gas and 100 sccm H₂ for 1 hour. (b) 0.1 sccm H₂ as the carrier gas and 100 sccm H₂ for 1.5 hour. (c) 0.2 sccm H₂ as the carrier gas and 100 sccm H₂ for 1.5 hour.
After the film growth, we characterized the hBN films by Raman spectroscopy. As we discussed in the experimental section, the optical contrast for hBN is much smaller than that for graphene. Thus, it is hard to identify the number of layers by naked eye or by analyzing the color contrast of the optical images. Nevertheless, there were characteristic peaks in the Raman mode for discerning the number of layers when the number was less than three layers.\textsuperscript{167} The hBN film was first transferred on to a SiO\textsubscript{2}/Si substrate after etching away the Fe foil by nitric acid. Figure 5.5 (a) shows the optical images of transferred hBN flakes prepared using the same conditions as described for Figure 5.4 (a). The monolayer hBN flakes are highlighted by the dash triangles. Moreover, Figure 5.5 (b) represents a complete hBN film with thick regions, grown under the same conditions as described in Figure 5.5 (b). We conducted the Raman analysis using a 532 nm laser on both samples and plotted the Raman spectra in Figure 5.5 (c). The peak for multi-layer hBN is located at \( \sim 1366 \text{ cm}^{-1} \), taken from the thick regions in Figure 5.5 (b). As the thickness decreases, the intensity decreases and the peak position show a blue shift, consistent with the previous report.\textsuperscript{167} The peak for monolayer is still discernible, occurring at \( \sim 1370 \text{ cm}^{-1} \), with a further blue shift relative to the bilayer hBN, in agreement with theoretical calculations.\textsuperscript{211}
Figure 5.5 Optical image and Raman spectra of CVD-grown monolayer hBN (black), bilayer hBN (blue) and multilayer hBN (red) using Fe as the substrate. The growth conditions for (a) and (b) are 0.1 sccm H₂ as the carrier gas /100 sccm H₂ for 1 hour, and 0.1 sccm H₂ as the carrier gas /100 sccm H₂ for 1.5 hour, respectively.
Moreover, in Figure 5.6, the AFM image for the hBN on the Fe substrate shows apparent large wrinkles. These wrinkles occur during the cooling process due to the negative thermal expansion coefficient of hBN\textsuperscript{210}, and the wrinkles remain on the SiO\textsubscript{2}/Si substrate after the transfer process. These wrinkles were measured to be approximately 4-10 nm high for the ~10 nm thick films and the wrinkle thickness increases in height with increasing film thickness. Additionally, the width of the wrinkles increase when increasing the film thickness. The variation in the total film thickness that results from wrinkling presents a challenge to graphene device fabrication, since h-BN wrinkles will result in a non-uniform electric field when used as a gate dielectric, and will induce surface roughness scattering when the hBN is used as a supporting substrate for supporting CVD or exfoliated graphene.\textsuperscript{14} The wrinkles were also observed in transferred CVD-grown graphene and the wrinkling can be significantly reduced by using a modified transfer process, which is currently being studied by Dr. Jin-Yong Hong in our group. We expect that similar modifications to the hBN transfer process may also help provide improved transfer morphology of CVD-grown thick hBN films.

Figure 5.6 AFM image of transferred multi-layer h-BN on a SiO\textsubscript{2}/Si substrate. (a) 2D height image. (b) The corresponding 3D height image.
To further study the structure and chemical composition of hBN films, we used transmission electron microscopy (TEM), EELS, X-ray photoelectron spectroscopy (XPS) and optical absorption. High resolution TEM was carried out using a Jeol 2010F and the results are presented in Figure 5.7 (a)-(c). The in-plane lattice constant is estimated to be around 0.25 nm, which is consistent with previous reports. The diffraction patterns also confirm the single crystal nature of the examined area, indicating a high quality of the grown hBN film. Figure 5.7 (b) shows TEM images of the edges of a suspended hBN film, allowing for the identification of the number of layers. The EELS measurement in Figure 5.7 (c) shows three peaks occurring at 180eV and 390 eV, corresponding to the characteristic K-shell edges of B and N, respectively. Also the EELS spectra confirms that the stoichiometric ratio of B to N is 1:1. We also performed XPS measurement on the hBN sitting on Fe foils. The binding energies of N1s and B1s are 398 eV and 191 eV, respectively, in agreement with a previous report. To investigate the optical properties, UV-visible absorption spectra of the hBN are presented in Figure 5.7 (e). The calculated optical band gap is found to be 5.86 eV.
5.1.3 Growth Dependence on the Fe Grains

We found that the morphologies of hBN films varies on different grains on Fe foils. As shown in Figure 5.8 (a), the low magnification SEM image shows that the morphologies of hBN films are distinguishably different in two grains, which are separated by dotted red lines. Most of the hBN films are triangles, consistent with previous reports. In contrast, in the triangular region, the hBN films show stripes. Figure 5.8 (b) shows SEM image of transferred hBN ribbons on TEM grid. We observed that the hBN ribbons are suspended over the holes. The width of the ribbons are about...
1~2 μm and the edges are very sharp. It should be noted that the brighter region in the upper right corner is also hBN ribbon but the film is much thicker. Figure 5.8 (d) shows the further TEM characterization at the same location. The inset picture shows the diffraction pattern taken from the hBN ribbons, indicating that these ribbons have the same crystal orientation. Further characterizations are needed to study the growth dependence on the grain orientations such as electron backscatter diffraction (EBSD), as we will discuss in Chapter 6.

Figure 5.8 Morphologies dependence of thick hBN on the grain orientations on Fe foils.
5.2 Synthesis of Hexagonal Boron Nitride on Pt

Monolayer hBN is very useful for a variety of applications, such as growth templates, tunneling barriers, and atomic membranes. Since the discovery of graphene, many layered materials have been explored and their atomic layer structures and properties were demonstrated by Scotch-tape method. However, some of these few layer materials are unstable under ambient conditions such as black phosphorous (BP), NbSe₂, MoTe₂ etc. For instance, few-layer BP degrades in air over a few days. The poor stability of these materials limits their experimental investigation and future application. Thus, it is important to find approaches for encapsulating these materials, while allowing further electrical characterizations. For example, we have found that by capping BP flakes with monolayer graphene, BP can be preserved in air for more than two weeks, in contrast to one to two days without encapsulation. This is because monolayer graphene is impermeable to oxygen and water and provides protection for BP against degradation in air. However, graphene is conductive, which hinders the investigation of the electrical properties of BP. Thus, monolayer hBN is more suitable as an encapsulating layer for BP. Monolayer hBN is impermeable to oxygen and water. Moreover, it shows a high tunneling conductivity vertically while being insulating in-plane, which provides opportunities for contacting BP with metal pads.

Figure 5.9 shows the optical images of transferred monolayer hBN on SiO₂/Si. The blue regions are monolayer hBN, and the homogeneity in color indicates a uniform monolayer hBN layer. Moreover, the Raman spectra of a CVD-grown monolayer hBN is comparable to a monolayer hBN obtained from Scotch-tape method, as shown in Figure 5.9 (b), suggesting a high quality of the CVD-grown hBN film.
Figure 5.9 Optical images and Raman spectra of monolayer hBN. (a) The optical images of a transferred monolayer hBN film on SiO₂ (300nm) /Si. (b) Comparison of the Raman spectra of CVD-grown hBN monolayer on Pt and a mechanically exfoliated monolayer hBN.

Additionally, we can prepare thick hBN grown on Pt. Recent works have reported synthesis of monolayer hBN using Pt. It is suggested that the growth rate of the hBN becomes extremely small after the formation of the first monolayer of BN due to the strong reduction of the surface reactivity; therefore, only monolayer hBN grows on the Pt substrate. Similarly, we can grow monolayer hBN at 1000°C or a lower temperature of 900°C. However, we observed that thick hBN can be obtained at a high temperature (1100°C). Figure 5.10 (a) shows a TEM image of an hBN film with low magnification and Figure 5.10 (b) presents the EELS measurement, indicating that the measured stoichiometric ratio of B to N is 1:1 measurement. High TEM resolution images taken from the edges of hBN in Figure 5.10 (c) shows that the hBN films are multilayers, and the number of layers can reach up to 10 layers.
Figure 5.10 TEM Characterization of thick hBN films. (a) TEM images of hBN films. (b) EELS mapping of the hBN at the same location. (c) Folded edges of hBN films taken from (a).

Moreover, we found a strong thickness dependence on the grain orientation of the Pt foils. Figure 5.11 (a) and (b) represents the optical image of the transferred hBN films grown on SiO$_2$/Si substrates. The films shows patches of different grains with sizes of about a few hundred microns. The brighter regions indicate that the film is thicker and vice versa. We found that the shape/size of the patches are the same as the grains on the Pt foil, indicating that the hBN growth is highly dependent on the grains on the Pt foil.

Figure 5.11 (c) shows the corresponding EBSD image, which allows us to correlate the thickness of the hBN to the crystal orientation of the Pt grains. The results show that thin hBN films prefer to grow on grains with the (001) orientation and thick films prefer to grow on grains with the (111) and (101) oriented regions. We will carry out following experiment to further study the growth behavior:
Figure 5.11 Correlation of the thickness of the hBN films and the grain orientation of the Pt substrate. (a) Optical images of a typical Pt foil. The dark lines indicate the grain boundaries. (b) Optical images of transferred hBN films on SiO₂ (300nm)/Si. (c) EBSD images of the same Pt foil. The highlighted regions represent the same grains.

AFM measurements were performed on the thick hBN film grown on the same Pt foil but different grain orientations. From Figure 5.12 (a) to 5.12 (f), the thickness of the hBN film increases. Figure 5.12 (a) shows an AFM height image of monolayer hBN prepared on a Pt foil, which has a very uniform thickness. In Figure 5.12 (b), there are some small domains, which are identified as the second layer on the complete monolayer hBN film. As the thickness increases, more wrinkles start to appear and we can observe a decreased crystallinity of these hBN films. For example, Figure 5.12 (f) displays a highly disordered film with small patches of domains and wrinkles.
Figure 5.12 AFM images of transferred hBN film grown on the same Pt foil but on different grains. From Figure 5.9(a) to 5.9(f), the thickness of the hBN film increases.

Chapter 6: Conclusions and Suggestions for Further Research

6.1 Thesis Summary

In conclusion, for the synthesis of bilayer graphene, first, we have demonstrated the growth of bilayer graphene using Cu enclosures. The bilayer graphene domain size achievable was more than 20 μm and the area coverage can reach 100%. This growth
method provides a facile tool to synthesize, both AB-stacked and turbostratic hybrid $^{12}\text{C}/^{13}\text{C}$ bilayer graphene. Utilizing this isotope labeling technique we are able to characterize not only the stacking orientation of our synthesized bilayer samples, but also the stacking sequence of our bilayer using Raman spectroscopy, thereby enabling us to have a deeper understanding behind the growth mechanisms involved in the bilayer graphene synthesis. It also serves as a rapid tool for characterizing the stacking information under various growth conditions and how they influence the stacking order.

Second, by inspecting the evolution of the two surfaces of the Cu enclosure during the LPCVD synthesis, we have gained a better understanding of the bilayer growth mechanism on the outside surface of the enclosure. It is concluded in this study that the two surfaces are coupled by carbon diffusion through the Cu foil. By identifying the pathways for methane gases and active carbon, we found that carbon diffusing through the Cu foil allows for a continual growth of bilayers from underneath the outside monolayer graphene. On the basis of the monolayer graphene growth on the inside surface and the inter-copper carbon diffusion process, we derived a growth model for the bilayer graphene growth on the outside surface, which agrees well with the experimental findings. Finally, we verified the validity of our model by measuring the thickness dependence of the Cu foil on the delivery rate of carbon. Moreover, utilizing intercatalyst diffusion pathways may serve as a more general method for the synthesis of other layer-by-layer hybrid structures, such as graphene on hBN or on isotopic bilayer systems. The improved understanding of the synthesis of bilayer graphene on copper catalysts will lead to the better control of bilayer graphene growth for future bilayer graphene-based devices and potentially for other bilayer nanomaterials.

Lastly, by applying the growth mechanism on the carbon diffusion, we reverse the direction of the carbon source from the outside to the inside in order to grow uniform bi-/multi-layer-free monolayer graphene with a W foil enclosed inside of the Cu enclosure, acting as the carbon sink. The bi-/multi-layers underneath the monolayer graphene are
selectively removed while the monolayer remains intact. The W foil plays an important role in maintaining a low carbon content inside of the Cu enclosure, by itself absorbing carbon. Both XRD and XPS results indicate the formation of W2C on the W foil. Finally, using double Cu enclosures, we were able to achieve uniform large-domain graphene growth with no bi-/multilayers. The formation of large-area single-domain monolayer graphene can enable large-scale integration of graphene devices with high yield and high reproducibility.

For the synthesis of hBN, Fe foils and Pt foils were used as the substrate. We found that both monolayer and thicker hBN can be obtained on these substrates. The thickness and the morphologies of the resulting hBN films are dependent on the growth conditions. For example, a higher flow rate or a longer growth time lead to thicker hBN films using Fe. Moreover, by increasing the growth temperature from 1000°C to 1100°C, thicker hBN can be achieved on Pt foils as well. By characterizing the films using Raman spectroscopy and TEM, we conclude that the films grown on Fe are of high crystalline quality; however, the films are not uniform in thickness. Further optimization of the transfer method is also needed to remove the wrinkles in the films in order to make the technique useful for future applications such as substrates for other 2D materials or dielectrics. On the other hand, uniform monolayer hBN can be prepared on Pt foil; however, as the thickness increases, the crystallinity decreases.

6.2 Suggested Further Research

6.2.1 Synthesis of Uniform Thick Multilayer hBN Films on Fe foil

Preliminary results have shown a thickness dependence on the crystalline orientation of Fe substrates. We will in the future carry out a systematically study of the growth behavior dependence on the crystal orientation of the metal substrate in detail to
deepen our understandings. Figure 6.1 shows that the hBN films prefer to start to grow on certain orientations. However, the results are not very accurate since we performed the EBSD after the hBN growth. hBN films are known as a good insulator; thus, the film may screen some information. Therefore, before the hBN growth, we need to mark the locations of certain grains and conduct EBSD to study the grain orientations. Then, we will carry out time dependent growth to study the evolution of the morphologies and thickness of hBN films.

![SEM and EBSD images of hBN on Fe foil](image)

Figure 6.1 Characterization of hBN on Fe foil by EBSD.

Furthermore, since the morphologies and the thickness of the hBN films varies on different grain orientations, to obtain a uniform hBN films, we need to have larger Fe grain size. We found that by annealing the Fe foil at 1100°C for a long time, the grain
size will increase. In Figure 6.2, the EBSD mappings show that after annealing the same Fe foil at 1100°C for 10 hours, the small domains emerge to form larger domains. However, since the results are limited, it is still hard to tell which orientation comprises the majority. Moreover, we expect that by annealing the Fe foil at a higher temperature such as 1500°C (the melting temperature of Fe is 1538°C), we can achieve a more uniform hBN film.

![EBSD mappings on the same locations of a Fe foil after high temperature annealing processes.](image)

**6.2.2 Synthesis and Characterization of Monolayer hBN**

It was reported that the hBN grown on the same Pt grain orientation has the same grain orientations. The researchers demonstrated that by coating a layer of liquid crystal on the hBN film, we can visualize the orientations of hBN using polarizing optical microscopy. However, we found that the results are not very consistent in our experiment. Thus, we want to use TEM to map out the orientations of hBN. TEM results are more convincing since we can see the orientations of the film directly. We have
developed a method to accurately mark the location of hBN on each grain. First, after hBN growth on Fe, we directly deposit a layer of Pt thin film (∼ 4 nm) using Helios, as shown in Figure 6.3 (a). Figure 6.3 (b) shows the optical image of the Pt foil, the marks can be observed on the hBN on Pt foil. After the bubbling transfer of hBN off the Pt foil, the marks are gone. Figure 6.3 (c) shows the SEM images of transferred hBN film on a TEM grid. The SEM images helps to locate the position of the marks. It is important to point out that the marks should be separated since it may be transferred onto the metal grid. Figure 6.3 (d) shows the corresponding TEM images of the same sample. Consequently, we can use SAED to characterize the grains of hBN.

Figure 6.3 Deposition of Pt marks on the hBN on Fe foils.
The thick hBN thin film can be used for encapsulating other 2D materials, in order to meet the needs of different groups. I am currently working with Xu Zhang and Yuxuan Lin from Professor Tomas Palacious in the same department for more electrical characterizations. In particular, we will use the monolayer hBN to encapsulate monolayer MoS$_2$, which is on top of thick multilayer hBN. (Figure 6.4) We expect that the sandwiched the MoS$_2$ will have enhanced performance.

Figure 6.4 Schematics of the proposed device. A monolayer MoS$_2$ is sandwiched by layers of thick (~15 nm) hBN films at the bottom as the substrate and a layer of monolayer hBN as the protective layer.
Appendix:

A.1 Certificate of analysis for Cu foil

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<th>Cr</th>
<th>K</th>
<th>Mn</th>
<th>Pb</th>
<th>Al</th>
<th>Bi</th>
<th>Cd</th>
<th>Fe</th>
<th>Mg</th>
<th>Na</th>
<th>Si</th>
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<td>99.9%</td>
<td>10</td>
<td>16</td>
<td>50</td>
<td>4</td>
<td>200</td>
<td>2</td>
<td>200</td>
<td>10</td>
<td>20</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>

Values given in ppm unless otherwise noted.

This document has been electronically generated and does not require a signature.
A.2 False-coloring and Percentage Calculation Process

A.2.1 Steps for False-coloring Process

Step 1: Open the original image (Figure A.1 (a)) using Gwyddion (a free image processing software). Go to Data Process-Level-Polynomial Background to extract and remove the background to get Figure A.1 (b).

Step 2: Open Figure A.1 (b) using Photoshop. Go to Image-Adjustment-Gradient Map to false color the images to get Figure A.1 (c). The RGB value and the color code used for each layer are listed in the table below.

Figure A.1 (a) The optical images of graphene films. (b) After processing the optical images using Gwyddion. (c) After false-coloring the images (b) using Photoshops.

Table A.1 The color code used for false-coloring the optical images of graphene films.

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<th>R</th>
<th>G</th>
<th>B</th>
<th>#</th>
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<td>254</td>
<td>fefefe</td>
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<td>141</td>
<td>c1748d</td>
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<tr>
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<td>52</td>
<td>7a1534</td>
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</table>
A.2.2 Steps for Percentage Calculation

Following Step 1 in the previous section, go to **Data Process-Mark Grains by Threshold**. By adjusting the threshold value, we can select the areas. Then go to **Grains-Statistics**, the pop-up window shows the percentage of selected area as well as the mean grain size.
Bibliography

K. Nat Mater; Basov, L.; Cheng, H. M.

Yang, W.; Kong, 72.


