Doctoral Thesis

Controlled Synthesis of Low Dimensional Carbon Nanomaterials via Chemical Vapor Deposition

Author(s):
Yang, Ning

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CONTROLLED SYNTHESIS OF LOW DIMENSIONAL CARBON NANOMATERIALS VIA CHEMICAL VAPOR DEPOSITION

A dissertation submitted to attain the degree of

DOCTOR OF SCIENCE of ETH ZURICH

(Dr. Sc. ETH Zurich)

presented by

NING YANG

M. Sc. Electrical Engineering,
University of Southern California
Born on May 8th 1991, citizen of China

accepted on the recommendation of

Prof. Dr. Hyung Gyu Park, examiner
Prof. Dr. John Robertson, co-examiner
Dr. Christos Emmanouil Frouzakis, co-examiner
Dr. Seul Ki Youn, co-examiner

Zurich, 2017
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Abstract

The discovery of carbon nanotubes (CNTs) and graphene over the last two decades has caused a phenomenal shift to the paradigm of dimensionality in materials science. CNT is a seamless cylindrical graphitic nanostructure (1-D) made of sp²-hybridized carbon atoms, whereas graphene is a two-dimensional (2-D) honeycomb lattice of the carbon atoms. Sharing the sp²-hybridized carbon atoms as a building block, these low dimensional nanostructures are fundamentally related.

The present thesis delves into the synthesis aspects of these low dimensional carbon nanomaterials – vertically aligned (VA-) CNT and bilayer graphene in particular – via chemical vapor deposition (CVD), through understanding and tailoring the partaking factors of the synthesis, and also by characterizing the properties of the resultant nanostructures.

Despite the tremendous advancement in the synthesis of VA-CNTs, the mechanism of diameter-controlled growth is not fully elucidated yet, and the average diameters of VA-CNTs are typically larger than 2 nm. Here, we carry out a decoupled investigation on the control of acetylene-based precursor thermal rearrangement and the catalyst-support interaction, to deepen the understanding of VA-CNT growth kinetics and achieve diameter-controlled VA-CNT growth.

In order to understand the effects of the gas-phase reactions on the growth kinetics of VA-CNTs, a systematic investigation is carried out in a temperature gradient (TG-) CVD setup. TG-CVD provides various thermal environments for the reaction of carbon feedstock (e.g., acetylene) in the chamber, producing various active carbonaceous reactant species atop the catalyst. We find out that the activation energy monotonically increases with respect to the acetylene partial pressure and with the acetylene pre-treatment temperature as well. We propose an analytical model assuming multiple reaction pathways, which takes into account the cumulative effect of the secondary acetylene-pyrolysis products on the surface reaction of the CNT formation. Our simulation results based on the proposed mechanism
agree well with our experimental data that cannot be explained simply by a single-rate-limiting-step-based kinetic model.

Furthermore, growth of VA-CNTs having sub-1.5-nm diameters is demonstrated by optimizing the interaction between catalyst and support. The alumina support is engineered in a sequential process: heat treatment followed by ion beam bombardment. The order of the alumina treatments is found out to be critical to the growth efficiency and the narrow distribution of the tiny CNT diameters. Supported by microscopic and spectroscopic evidence, we scrutinize the influence of the alumina surface properties on the evolution of catalysts and hence postulate the positive contribution of alumina to the diameter-controlled growth of CNTs upon acquiring distinctive surface and bulk properties.

The second part of this thesis presents extensive investigation results on the graphene growth mechanisms and structural control. It has been previously claimed that the growth of monolayer graphene grown on copper by CVD is a self-limiting process and follows a sigmoidal growth kinetics, controllable with adsorption-desorption dynamics and the dispersive kinetic processes of catalytic dissociation and dehydrogenation of carbon precursors atop copper. However, monolayer graphene is a semimetal with no bandgap, limiting its potential applications. AB-stacked bilayer graphene, on the other hand, has been reported to have a tunable bandgap under electric fields and thus attracted enormous attention. With the acquired knowledge on the growth mechanism of monolayer graphene, we report a systematic investigation on the kinetics and termination mechanisms of bilayer graphene on copper using a growth-and-regrowth method. In this regrowth method, the secondary graphene layers already nucleated along with primary layers expand selectively, whereas enlargement of the latter is inhibited, ascribed to the hydrogen-termination of the layer edge as well as the oxidation of the nearby copper surface. We observe, for the first time, the selective secondary-layer growth to follow the sigmoidal kinetics. Our observations support the postulate of a time-dependent transition from diffusion-limited to reaction-limited regimes and identify the mechanistic disparity between the growth of the first and the second layers.
Overall, this thesis offers the understanding and tailoring of many aspects of the VA-CNT and graphene growth and also provides the property characterization results of the resultant nanostructures. Successful development out of this thesis could lend the combined method of TG-CVD and alumina treatment immediate adaptability to industrial application of ultranarrow VA-CNTs. It will also help devise rational design, through a regrowth method, for large-scale synthesis of bilayer graphene of high AB-stacking ratio.
Zusammenfassung


Um die Auswirkungen der Gasphasenreaktionen auf das kinetische Verhalten von KNR zu verstehen, wurde eine systematische Untersuchung mittels Temperaturgradienten (TG-)CVD durchgeführt. TG-CVD stellt verschiedene thermische Umgebungen für die Reaktion von Acetylen-Vorstufen in der Kammer her, was in verschiedenen Kombinationen von aktiver kohlenstoffhaltiger Reaktantenspezies
über dem Katalysator resultiert. Wir konnten im Zuge der Laborversuche beobachten, dass die Aktivierungssenergie in Bezug auf den Acetylen-Partialdruck monoton ansteigt, insbesondere dann, wenn die Ausgangsgase bei hoher Temperatur vorgewärmt sind. Ein analytisches Modell mit mehreren Reaktionswegen, das die kumulativen Auswirkungen der sekundären Acetylen-Pyrolyseprodukte auf Oberflächenreaktion für das Wachstum von KNR beschreiben kann, wird vorgeschlagen. Unsere Simulationsresultate, die auf dem vorgeschlagenen Mechanismus basieren, stimmen im Gegensatz zu den einfachen, rate-limitierten kinetischen Modellen gut mit den experimentellen Daten überein.


## Nomenclature

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>APCVD</td>
<td>Atmospheric Pressure Chemical Vapor Deposition</td>
</tr>
<tr>
<td>(C)CVD</td>
<td>(Catalytic) chemical vapor deposition</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscattering Diffractometry</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>HAADF</td>
<td>high-angle annular dark field</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
</tr>
<tr>
<td>LEEM</td>
<td>Low Energy Electron Microscope</td>
</tr>
<tr>
<td>LPCVD</td>
<td>Low Pressure Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MS</td>
<td>Mass Spectrometry</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>$(n,m)$</td>
<td>Single walled carbon nanotube chiral axes</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>PMMA</td>
<td>(poly methyl) methacrylate</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area (electron) diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>VA-CNT</td>
<td>Vertically Aligned Carbon Nanotube</td>
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1 Introduction

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1.1 Brief Overview on Low Dimensional Carbon Nanomaterials

The carbon element has been widely studied because of its extremely versatile behavior in physics, chemistry and biology. Carbon atoms can bind with each other to form strong covalent bonds in 1-, 2- and 3-D networks [1]. This enables them to form diatomic molecules, through to nearly infinite polymers and crystals with remarkably different properties. The best known forms of carbon are graphite, diamond and amorphous carbon. Graphite is one of the softest materials known, owning planar atomic sheets (graphene) within which carbon atoms form a two-dimensional network of six-membered conjugate rings with a C-C bond length of 1.42 Å. There is a very limited interaction between neighboring sheets, so they loosely bond with each other by a distance of 3.35 Å [2, 3]. In contrast, diamond is the hardest material, having pure sp³ covalent bonding and highly symmetrical unit cell [4]. Amorphous carbon is free, reactive carbon that contains mixed states of sp² and sp³ hybridized bonds [5]. Until the last few decades, the knowledge of carbon allotropes expands to low dimensional materials such as fullerene, carbon nanotube and graphene (Figure 1.1) [6].

Fullerenes are a zero-dimensional (0-D) form of graphitic carbon, arranged in pentagons and hexagons, forming the structure of a hollow sphere, tube and many other shapes [7]. Carbon nanotubes (CNTs) belong to the fullerene family of carbon allotropes. They are cylindrical molecules of sp²-hybridized carbon atoms arranged in a honeycomb structure [8]. These cylindrical structures could be generally grouped
into categories of single- and multi-walled CNTs. As the name suggests, single-walled CNTs (SWCNT) compose one atom layer of graphene rolled up into a cylindrical structure. The resulting SWCNT can be described by a “chiral” vector (n,m), where n and m are unit vectors in two directions along the honeycomb structure of the graphene sheet \[9\]; whereas multi-walled CNTs (MWCNTs) contain multiple tubes in concentric cylinders. MWCNTs generally have a larger diameter (5 to 20 nm) than SWCNTs (0.8 to 2 nm) \[10\]. CNTs are usually a few nanometer wide, but extending from less to a micrometer to several millimeter in length. The high aspect ratio (i.e., length to diameter ratio) of CNTs approaches a one-dimensional (1-D) structure.

Figure 1.1 The world of synthetic carbon allotropes. In this family, fullerenes represent the most intensively investigated class. The first fullerene-based products such as organic solar cells have already entered the market. The material properties of the carbon nanotubes and especially those of graphene are considered to be even more promising. However, it is still difficult to control their chemistry and also the bulk production of uniform monodisperse samples; adapted from ref. \[11\].

Graphene is another allotrope of carbon, consisting a flat monolayer of carbon atoms tightly packed into a two-dimensional (2-D) honeycomb structure \[12\]. The 2D crystals were once presumed not to exist because they are thermodynamically unstable. Till 2004, graphene crystals were obtained on top of non-crystalline substrate by
Novoselov, Geim and co-workers through an easy isolation method [13]. Since its first isolation, graphene has been widely studied and shown to possess unique properties such as extremely large charge mobilities up to 1,000,000 cm²V⁻¹s⁻¹ [14-17], broadband optical transparency, linear dispersion resulting in massless Dirac fermions [12, 18, 19], a near-zero intrinsic bandgap resulting in saturable optical absorption [20], tunable bandgap [21], unprecedented mechanical strength (1 TPa tensile modulus) [22] and one of the highest thermal conductivities ever reported (5300 W·m⁻¹K⁻¹) second only to superfluid He [23].

1.1.1 Vertically Aligned CNTs

CNTs exhibit extraordinary electrical, thermal and mechanical properties, owing to their unique molecular structure [24]. The hollow structure of CNTs contributes to the low mass density and high tensile strength and Young’s modulus, which is far superior to typical steel. Also, CNTs possess extreme high thermal stability and conductivity. CNTs are reported to be stable up to 2800 °C in vacuum and 750 °C in air; and the heat conduction rate (SWCNT 1750-5800 W·m⁻¹K⁻¹, MWCNT 3000 W·m⁻¹K⁻¹) is comparable to that of diamond (3320 W·m⁻¹K⁻¹) and 1 order of magnitude higher than that of copper (385 W·m⁻¹K⁻¹) [25]. In addition, CNTs own extraordinary electric properties. Depending on the structure of CNTs, they can be either metallic or semiconducting, which is meaningful for both application in electronics as transistors and the current-carrying wires. As current-carrying wires, metallic CNTs can sustain current density up to one hundred fold higher than copper wires [26]. As semiconductors, CNTs could offer variable bandgaps up to 2 eV [27]. These fascinating properties of CNTs have made CNTs very attractive for a variety of advanced applications, including composite materials [28], batteries [29], capacitors [30], field emission displays [31], transistors [32], sensors [33] and membranes [34] etc.
The CNT industry consists multi-level hierarchy (Figure 1.2). On microscopic scale, it involves catalytic reactions in which carbon atoms assemble into a 1-D CNT structure; while on the macroscopic scale, the properties and structures of CNTs can be influenced by factors such as transport phenomena in the reactor [35]. For most applications, it is most desirable to have CNTs with high purity, low cost, provides well-defined large surface area and are readily incorporated to device configuration [36]. To serve these requirements, vertically aligned CNT (VA-CNT) “forest” are particularly suitable. VA-CNTs comprises tens of thousands of CNTs per square micrometer, which are self-assembled on a substrate. The high packing density of VA-CNTs provides effective solution for the requirements for the efficient manufacturing of CNTs. VA-CNTs are usually synthesized by chemical vapor deposition (CVD) method. CVD is the most controllable, scalable and efficient method for VA-CNT growth [35]. VA-CNTs were first grown using Fe as catalyst on SiO$_2$ support via chemical vapor deposition (CVD) by Li in 1996 [37]. Initially the VA-CNTs were MWCNT with an average diameter of around 30 nm. After two decades of intense efforts, single-walled VA-CNT could be produced efficiently on Fe catalysts supported by Al$_2$O$_3$ [38]. However, further shrinkage of the diameter without losing the alignment of VA-CNTs is still challenging.
The diameter control of VA-CNTs, especially in the SWCNT regime, is essential for many applications and yet a long-standing challenge. In electronics applications, SWCNTs of different diameter and chirality have different band structure [39]. One way to confine the chiral distribution is to shrink the diameter distribution of CNTs. The specific chirality of certain diameter CNT is normally determined by the product’s relative stability. In other words, the control of diameter and chiral distribution are closely related in electronics applications. In membrane applications, pore size and diameter play a key role in the ion rejection efficiency. According to molecular modeling, the salt rejection capacity decreases (100% to 58%) drastically with increasing pore diameter (0.32 to 0.75 nm). Ideally, CNTs used for membrane application should have diameter around 0.6 nm [40].

Unfortunately, attempts to control the diameter of VA-CNTs in the regime below 1 nm have not been successful so far. It is generally believed that the diameters of CNTs are determined by the size of the catalytic metal nanoparticles for metal-catalyzed CNT growth by CVD. The nanoparticles play two important roles during CNT growth: as a catalyst for chemical reactions and nanoscale template for the nucleation and growth of CNT. As a catalyst, the nanoparticles are responsible for the absorption and dissociation of gaseous precursor, diffusion of carbon intermediates and their chemical interactions [36]. However, metal nanoparticles are extremely sensitive to coarsening at CVD temperatures in the sub-nm regime, due to thermal instability. Second, the small sized catalyst nanoparticles are more vulnerable to carbon poisoning and subsurface diffusion [41]. In a nutshell, the vulnerability of nanoparticles to factors like coarsening, carbon encapsulation and subsurface diffusion, has hindered the advancement of CNT growth in this diameter regime.

1.1.2 Graphene

Most investigations on the fundamental properties of graphene have been carried out using mechanically exfoliated graphene from highly oriented pyrolytic graphite (HOPG) or kish sources [13]. The high graphitic quality and cleanliness of this method have provided a crystallographically ideal material perfectly suited for a test bed for fundamental exploration. Indeed, graphene obtained from this method is what has allowed to measure many, if not all, of the above properties
in practice. However, exfoliation techniques can only provide micron- and sub-micron-sized graphene crystals at random and uncontrolled locations. Despite a wide variety of chemical and mechanical exfoliation techniques available and compatible with an arbitrary range of substrates, such approaches are unsuitable for technological purposes due to issues with scaling and reproducibility (Figure 1.3).

**Figure 1.3** Comparison of several methods for mass-production of graphene, which allow a wide choice in terms of size, quality and price for any particular application; adapted from ref. [42].

Given the unquestionably large catalogue of excellent mechanical, optical and electronic properties demonstrated, graphene is evidently a very promising material for a lot of technological applications such as flexible transparent conductors [43, 44], integrated circuit elements [45], high-frequency (GHz) transistors [46-48], ultracapacitors [49], battery electrodes [50, 51], porous membranes for filtration [52-54].
and desalination [55], passivation layers [56, 57], catalytic support [58], plasmonic sensors [59] and composite materials [60]. All of these applications require large area graphene produced via scalable, economical means. Thus, alternative isolation methods to mechanical cleavage are in critical need, with particular interest in direct chemical synthesis (Table 1.1). One example of this alternative approach is to use other top-down methods based on chemical exfoliation [61] which employ agitation of intercalated graphite or chemical reduction of graphene oxide in order to produce large quantities of crystal that can coat extremely large surfaces [43, 62] if coupled with various mechanical deposition techniques such as casting, spray casting, Meyer rod, Langmuir Blodgett, screen printing, and electrophoretic deposition. However, the resulting layer is an ensemble of graphitic material that is far from having the high quality (and subsequent properties therein) of the graphene monolayer, ascribed to the out-of-plane inter-flake connectivity, tunnel barrier dominance, and altered chemical structure. As such, atomistic (or bottom-up) synthesis methods are the sole option to obtain high quality continuous monolayers of graphene.

Early work on graphene synthesis focused on epitaxy of SiC by removal of the Si atoms from the crystalline surface. This method became popular among researchers because of the high quality of graphene obtained [63-66] and has been used to demonstrate some of the fastest GHz circuits ever produced [67]. Unfortunately, the SiC substrate is particularly expensive, confining the commercial feasibility to specialized applications such as very high performance electronics. Moreover, the Si sublimation process requires quite high temperatures (ca. 1500 °C) making the epitaxial growth incompatible with many substrates as well as further increasing the per-area cost of the synthesized material. Direct chemical assembly of benzene sub-units, as well as material properties thereof, has also been investigated [68, 69]. Although the feasibility of this promising approach has been evidenced, use of this synthesis method remains limited because of poor areal coverage and graphitic quality. More efforts are ongoing to overcome these issues.
Perhaps the most industrially viable approach is chemical vapor deposition (CVD) on catalytic metal substrates. CVD of graphene is emerging as the preferred method of synthesizing graphene for almost all applications, attributed in part to wide process window, large-area compatibility, and technical familiarity to the semiconductor industry processes. Early CVD processes employed transition metal substrates such as Ir [78, 79], Ru [80, 81], Pt [82], Pd [83], and Ni [70, 71] with exploiting the high carbon solubility of these metals to precipitate carbon from the supersaturated solid-solution reservoir in their bulk lattices to form graphene layers on their surfaces. Among them, Ni has been received favorable recently. Nevertheless, the cost of some of
these high purity catalysts, especially Ir, coupled with difficulties in controlling the number of precipitated layers has urged researchers to search for metals with lower carbon solubility. More recently, Cu has proven to be the most widely adopted substrate for producing polycrystalline graphene monolayers [84, 85]. State-of-the-art Cu-based CVD graphene has been evolved to the extent that it is now extremely graphitic in nature, and approaches a point where it can yield almost as good electronic quality as an individual graphene flake exfoliated mechanically [72-76] while capably scaled to hundreds of meters by emerging roll-to-roll processes [77].
1.2 Thesis Structure

This thesis charts the author’s work on the development of controlled synthesis of CNT and graphene using CVD, with an emphasis on small-diameter VA-CNTs and AB-stacked bilayer graphene.

Chapter 1 presents an introduction to carbon nanotubes and graphene, including their properties and potential applications.

Chapter 2 focuses on the state of the art of catalytic CVD towards controlled synthesis of VA-CNTs and graphene. For VA-CNTs, even though limitations in the reduction of the diameter VA-CNTs to sub-nm still exist, significant improvements in diameter control have been accomplished by optimizing the pretreatment conditions, CVD growth conditions and catalyst design. For graphene, two types of growth mechanisms, by carbon precipitation and surface adsorption, are compared. The important aspects of substrate preparation and graphene transfer have been summarized.

In Chapter 3, we study the growth kinetics of VA-CNTs by analyzing the critical parameters in the catalytic CVD process. We carry out a systematic investigation on the impact of gas precursor thermal rearrangement on the chemical composition of the gas products and the VA-CNT growth dynamics. An analytical model with multiple parallel pathways is proposed, which can relate the effects of acetylene pyrolysis products and the surface reaction process, thereby explaining the deviation of the Arrhenius slope of the CNT growth rate.

In Chapter 4, diameter-modulated, high-quality VA-CNTs with average diameter smaller than 1.5 nm are synthesized on a facile Fe-alumina catalyst design, with engineered alumina. The engineered oxide support - alumina - was first treated by heat and then by ion beam bombardment. The order of these alumina treatments is found to be important, and alternation of the alumina treatment sequence detrimental the growth efficiency.

Chapter 5 presents the current understanding of the growth mechanism for monolayer graphene and introduces a simple regrowth method for the synthesis of AB-stacked bilayer graphene. A reaction mechanism taking into account the competition between hydrogen and
carbon adatoms diffusion and carbon incorporation into graphene is proposed to describe the growth behavior of secondary layer graphene.

This thesis is concluded in Chapter 6 by summarizing the results and findings. A concluding overview of the findings is presented, followed by an outlook for future prospects of the field.

In summary, this dissertation dedicates to the controlled synthesis of two major carbon nanomaterials - CNT and graphene - by CVD. For each material, our approach begins with understanding the fundamental mechanisms and growth kinetics of the synthesis process, with a goal to maximize the growth efficiency, and continues to realize the structural control of the material through the optimization of CVD parameters or catalyst design.
2 Review on the Controlled Synthesis of VA-CNTs and Graphene via Chemical Vapor Deposition

Parts of this chapter have been published in:


2.1 Abstract

CNT and graphene both possess remarkable properties due to their unique 1-D and 2-D structures. Nevertheless, their utilization is often limited by their controlled growth. So far, numerous methods have been proposed to synthesize CNTs and graphene. Among those methods, catalytic CVD is currently the prevailing synthesis method of CNTs and graphene due to the controllability, low cost and scalability. In this chapter, we review the current effort towards controlled CVD of VA-CNTs and graphene. In the VA-CNT section, we discuss the diameter control of VA-CNTs by three methodologies: 1) influencing the diameter of CNTs through catalyst pretreatment by optimizing the annealing condition; 2) diameter control through CVD parameter optimization and 3) through catalyst design. In the graphene section, we review graphene synthesis via CVD, with particular reference to Cu-catalyzed CVD. An insight on the precipitation-based CVD synthesis is firstly given, followed by underlying surface catalysis. Subsequently, important aspects of graphene transfer and cleanliness are explained, and the efforts toward transfer-free direct growth on insulators are summarized. Next, the quality of CVD graphene and the film quality implications on the growth conditions are discussed. Lastly, the recent scale-up schemes for the mass-production are presented.
2.2 Controlled Synthesis of VA-CNTs

2.2.1 Catalyst Pretreatment

Catalyst pretreatment is a critical process for the controlled synthesis of CNTs, since it strongly influences the formation of nanoparticles and reduces the catalyst into active state. Usually, metal nanoparticles are formed by dewetting a thin film deposited on an oxide support layer. At elevated temperatures, the metal film is prone to dewetting into islands on the support due to its higher surface energy than that of the support material (Fig 2.1) [86, 87]. This dewetting process is driven by thermodynamics of minimizing the surface free energy at the catalyst-support interface [88]. For metal-catalyzed SWCNTs synthesized by CVD, it is generally believed that the diameter of the SWCNT product is governed by the size of the catalytic nanoparticles. The diameter and chiral distribution of CNTs could be narrowed by optimizing the pretreatment condition [89]. Moreover, the catalyst is reduced into metallic state in pretreatment process [90]. During annealing step, the catalyst will be exposed to a gas reductant. Both the gas composition of the reducing gas and the pretreatment condition (temperature, time, etc.) influence the oxidation state of the catalyst and consequently the nucleation efficiency of CNTs and catalyst-support interactions.

![Figure 2.1](image)

Figure 2.1 Schematic representation of the synthetic process for the SWCNT forest from metal catalysts; adapted from ref. [87].

2.2.1.1 Carrier Gas Composition

The carrier gases usually consist of an inert gas and a reducing agent. H\textsubscript{2} [91] and NH\textsubscript{3} [92] are the most widely used reducing agents in thermal annealing. In order to achieve efficient growth of small-diameter CNTs, the appropriate concentration of the reducing agent is crucial. Hofmann et al. have shown that the nanoparticles need to be at its metallic state in order to be catalytically active for CNT growth.
Oxides, and hydroxides of Fe, Co, and Ni can usually be reduced by H$_2$ and NH$_3$ [93]. The presence of the reducing agent during the catalyst annealing enables the particles to catalyze the hydrogenation of carbon [94].

**Hydrogen**

Considerably higher areal density of CNTs is observed after annealing in H$_2$ than in an inert atmosphere. In the inert atmosphere, the formation of nanoparticles is unfavorable, and the catalyst typically yields no CNT or CNTs at low density. The presence of H$_2$ is crucial to break down the catalyst thin film to tiny particles and reduce the catalyst oxides. It has been revealed that under reducing conditions, as the catalyst surface energy increases, catalyst particles have decreased mobility on the oxide layer caused by the strong interaction between the metal and the support [95], thereby dwindling the stable particle size. NH$_3$ is known to be a stronger reducing agent of organic materials than H$_2$. In this case, it is possible to carry out the NH$_3$-annealed CNT growth atop catalyst samples exposed to air for a long period of time up to a few months, whereas H$_2$ requires freshly deposited catalyst film within a few days [96]. Recently, Fouquet et al. have reported that applying NH$_3$ during the annealing could also narrow down the diameter range and chiral distribution of CNTs, by influencing the faceting/reconstruction of catalyst particles [89]. However, the N content in CNTs increases extensively by introducing NH$_3$. In order to avoid the unwanted N doping of CNTs, H$_2$ is considered as a cleaner reducing agent and is more widely applied in the research community [97].

**Hydrogen with additives**

A small amount of additives could be added in H$_2$ during the catalyst pretreatment. Chen et al. have observed a narrow diameter distribution of tiny CNTs and prolonged the growth lifetime by mixing a small amount of CH$_4$ with H$_2$ [98]. They suggested that CH$_4$ deposits a small amount of C on Fe particles, which possibly reduces the surface energy of Fe and prevents the coarsening of the Fe nanoparticles. Amama et al. have proposed that a small concentration of H$_2$O mixed with H$_2$ during the annealing can actually prolong the catalyst lifetime by impeding the Ostwald ripening of the catalyst [99].
2.2.1.2 Process Parameters during Pretreatment

Pretreatment Temperature

At an elevated temperature, the surface migration of the catalyst tends to be vigorous, enlarging the nanoparticles. Diffusion of the particles stems from variation in their shape, which could be induced through the evaporation and condensation of atoms onto the particle, migration of vacancies inside of the particle, and atom migration onto the surface. As temperature increases, catalyst atoms at defects first become mobile; then these atoms increase mobility; finally, at melting temperature, the mobility is so high that a liquid phase results [96]. In contrast, below certain pretreatment temperature, the catalyst yields no CNT, possibly due to insufficient reduction of the catalyst particles.

Pretreatment Time

Figure 2.2 Illustration of the catalyst particle evolution model during the reduction step; adapted from ref. [100].

The evolution of catalyst nanoparticles follows a time-variant mechanism with many processes involved. Schweiger et al. have analyzed the evolution of nanoparticles in four stages (Figure. 2.2): during stage I, the diameter of nanoparticles increases owing to Ostwald ripening promoted by the high areal density of the particles;
in stage II, the diameter decreases due to inward diffusion of catalyst into substrate; in stage III, the diameter decreases because of the reemergence of catalyst on the surface; finally in stage IV, Ostwald ripening becomes a dominant process, resulting in an increase of the particle diameter [100]. It is critical to find the sweet spot for the annealing condition to ensure the smallest diameter and high density of CNTs.

*Ramp Rate*

Other parameters such as the temperature ramp rate could also influence the CNT growth. Patole *et al.* have observed the decrease in CNT growth rate as ramp time rate decreases [101]. Gao *et al.* have demonstrated that controlled catalyst diffusion into the support in the pretreatment state by means of fast-heating is key to extending the Fe catalyst lifetime [102]. Ideally, the ramp time could be minimized by inserting the sample directly into the reactor at the growth temperature.

To sum up, the reduction and phase change of catalyst is accompanied by the reconstruction of the catalyst from a thin film into nanoparticles during the annealing. Both reduction and reconstruction of the catalysts depend on the reducing gas environment, temperature and the exposure time.

### 2.2.2 CVD Parameters

Following the pretreatment process, catalyst nanoparticles are exposed to gaseous hydrocarbon precursors at elevated temperatures for the nucleation and growth of CNTs. Initially, a certain initial population of catalyst particles nucleate to form CNTs in random directions. As the nucleation density increases, CNTs begin to align. When the number density of CNTs exceeds a critical threshold, CNTs grow collectively in a vertically aligned manner. The critical threshold depends upon the diameter, length and interaction of CNTs. In order to grow CNTs continuously without interruption of the precursor gas supply, it is important to maintain the interfaces between the catalyst particle and the precursor gas as well as between the catalyst and the solid CNT material. As CNTs continue to grow, amorphous carbon could be deposited on the catalyst nanoparticles, which blocks the interface of
the catalyst with the precursor gas, causing the catalyst deactivation and the growth termination of an individual CNT. Then, the collective growth of VA-CNTs proceeds with a slow decay of CNT density, resulting from the accumulation of growth termination of individual CNTs. As the CNT density falls below the aforementioned critical threshold, the collective growth of VA-CNTs comes to an end.

Interestingly, only a fraction of nanoparticles become active and nucleate CNTs (less than 12%) [103]. Whether the larger or smaller particles are able to nucleate CNTs strongly depends on the CVD parameters [104]. In this section, we discuss the impact of the CVD parameters on the properties of as-grown VA-CNTs.

### 2.2.2.1 Carbon Precursor Composition

A large number of carbon-containing molecules could be used as precursor or carbon feedstock for the catalytic growth of CNTs (e.g. acetylene, ethylene, methane and ethanol). The thermodynamic stability is an important feature of the precursor. Methane is highly stable, and does not decompose exothermally. The pyrolysis of CH$_4$ is only thermodynamically allowed at temperatures as high as 1000 °C or above it. In contrast, C$_2$H$_2$ and C$_2$H$_4$ and C$_2$H$_5$OH have little thermodynamically restriction for decomposition; and once provided with sufficient activation, can perform pyrolysis into atomic carbons, linear dimers and a large variety of organic compound and polycyclic aromatic hydrocarbons [105]. The stability of the carbon precursor could also be reflected by its chemical bonds. The strength of C-H bonds increases with decreasing number of C neighbors [106]. A similar trend can also be observed in a C-metal bond. It is worth noting that elements contained in precursors other than C, such H and O, are not a compulsory element for the growth of CNTs. Zhong et al. have revealed that C$_2$H$_2$ is the main growth species for VA-CNTs in both plasma assisted and thermal CVD [107]. Regardless of the original carbon precursor (CH$_4$, C$_2$H$_2$, C$_2$H$_4$ or C$_2$H$_5$OH), the precursor will be converted into C$_2$H$_2$ for the growth of CNTs in a large range of CVD processes. Here, we focus on C$_2$H$_2$-based growth.

The partial pressure of C$_2$H$_2$ influences the range of active catalytic nanoparticles and the diameter distribution [104]. After the pretreatment, the as-deposited catalyst thin film dewets into a large
number of particles of various sizes. At any given growth condition, there is an ideal dimension of nanoparticles to nucleate CNTs. The farther the nanoparticle size is away from the ideal value, the less likely such a nanoparticle can nucleate a CNT. Smaller particles have higher catalytic activity but are more vulnerable to catalyst poisoning at large carbon fluxes; larger particles are less likely to be poisoned but are more prone to being underfed by carbon precursor and does not nucleate CNT at lean carbon feeding [108]. These findings suggest that \( \text{C}_2\text{H}_2 \) partial pressure should be tailored low enough to enable the nucleation of small-diameter VA-CNTs.

During the CNT growth, a trivial amount of \( \text{H}_2\text{O} \) is often introduced in the CVD process to improve the growth lifetime and uniformity of CNTs [101]. \( \text{H}_2\text{O} \) has also been reported to increase the growth window and the catalyst tolerance to variations in the process gas composition. Furthermore, \( \text{H}_2\text{O} \) as an additive could inhibit Ostwald ripening in the SWCNT growth, due to ability of oxygen and hydroxyl species to reduce diffusion rates of catalyst atoms [99]. Nevertheless, excessive or uncontrolled amounts of \( \text{H}_2\text{O} \) could result in transients during the CVD process, harming the run-to-run growth consistency. In this scenario, Li et al. have proposed to move the catalyst in and out rapidly with a transfer arm, enabling the catalyst to be exposed only to stabilized gas compositions and thus improve the run-to-run consistency [109].

### 2.2.2.2 Growth Conditions

**Growth Temperature**

The growth temperature determines the catalytic activity of the particles. At high growth temperature, CNTs have higher growth rate because of accelerated catalytic decomposition of carbon precursor on the catalyst and of enhanced diffusion of carbon on the surface as well as in bulk catalyst particles. As the temperature increases beyond its optimal value, the growth rate deteriorates partly because of catalyst deactivation [110]. In addition, the temperature influences the evolution of the catalyst nanoparticles through Ostwald ripening and subsurface diffusion. Researchers have observed that higher temperature favors CNTs of larger diameter with a wider distribution. On the other hand, others have proposed that at high temperatures, the growth of small-diameter CNTs would be preferred because of the
curvature (diameter)-dependent thermodynamic stability of the nucleation cap of CNTs [111]; according to them, the smaller the diameter, the higher strain energy needs to be overcome and thus possesses the higher energy of formation.

_Growth Time_

The range of variation mediated by growth time is limited after the initial nucleation of CNTs. For example, Youn _et al._ have reported that VA-CNTs broaden their diameters from an initial value of 1.43 nm to 1.87 nm after 60 mins of growth [104]. Such changes in diameter with growth time can be attributed to the surface evolution (continuous migration and coalescence, Ostwald ripening, and subsurface diffusion) and the deactivation of the catalyst nanoparticles.

### 2.2.3 Catalyst design

#### 2.2.3.1 Catalyst Composition

The catalyst nanoparticles play at least two main roles in the growth of VA-CNTs: one is to accelerate chemical processes, such as dissociation of adsorbed molecules on the metal surfaces of the catalyst, by lowering their activation barriers; the other is to act as the template for CNT. Recent years have found many elements suitable for catalyzing the CNT growth. Basically, any type of Fe compounds could be used as a catalyst to grow SWCNTs after reconfiguration into Fe particles by proper hydrogen pretreatment [87]. Widely used catalysts today for VA-CNT growth are transition metals such as Fe, Ni, and Co.

It is generally accepted that a good catalyst needs to have a moderate solubility of carbon and great catalytic activity. In other words, the bond strength of the catalyst to adsorbates should not be too strong, so that products could be readily released after the catalytic reaction; simultaneously, the bond strength should not be too weak for the catalyst to dissociate the adsorbed species (Figure 2.3a). The catalytic activity of transition metals across the periodic table can also be described by a “volcano plot” or Brönsted–Evans–Polanyi (BEP) relation (Figure 2.3b) [112-114]. In addition to the activity, the catalyst should provide a sufficient particle number density to enable self-organized growth of a CNT forest through a “crowding effect.” Here,
aggregation of nanoparticles could incur in-situ diameter enlargement and cease of the growth.

**Figure 2.3** (a) schematic of carbon atoms on metal surfaces across the transition metal series, (b) Reaction rate (turnover frequency) vs. metal d orbital energy $E_d$, adapted from ref. [112].

Bimetallic catalysts were found to create a synergistic effect in the growth of VA-CNTs, displaying a higher activity than individual elements show [115]. Notably, non- or less active elements (Mo [116, 117], Cr [118], Cu [119]) are often mixed with catalytic active elements (Fe, Co) to prevent the aggregation of catalytic active nanoparticles. For example, Mo readily forms carbide with carbon, functions as a sink of carbon atoms and thus controls the feed rate of carbon to the active Fe or Co catalyst. Xiang *et al.* have observed that the diameter of VA-CNTs could be modified by changing the amount of Co and Mo in a binary catalyst system [117]. While increasing the Mo catalyst content by 5 times, the average diameter decreased from 2.5 nm to 1.2 nm. Later, Youn *et al.* have revealed that the deposition order of two metals, Fe and Mo, significantly affects the interaction and evolution of the bimetallic catalyst, where Fe-on-Mo type metal films develop to denser and smaller nanoparticles with prominent bimodality in size [116]. Recently, Cui *et al.* have reported sub-nm growth of VA-CNTs from a Co-Cu catalyst [119]. However, this paper has ambiguity in the diameter data drawn from TEM images that cannot completely exclude
a possibility that two or more CNTs overlap with each other in the image to mislead the analysis.

2.2.3.2 Catalyst Preparation Method

One common technique of preparing the catalyst for the growth of VA-CNTs is physical vapor deposition (PVD). A very thin film of Fe, Co, or Ni is deposited on a flat substrate using evaporation or sputtering. The film thickness is monitored by a quartz oscillator and varies from sub-nm to a few nm. Key parameters of the produced SWCNTs can be adjusted by tailoring the catalyst deposition process. For example, Na et al. have applied very slow deposition (8.1 pm s\(^{-1}\)) in order to deposit dense catalyst islands that covered the surface incompletely, enabling CNT growth on a TiN layer at a low temperature of 400 °C [120]. Zhang et al. have applied a direct current plasma treatment onto a Fe catalyst, which deposited a thin layer of carbon onto the catalyst and suppressed the sintering of catalyst nanoparticles [121]. The plasma treatment applied on Fe has improved the areal density of VA-CNTs over 8 times, compared with standard conditions. In order to serve for applications that require non-planar structures, Chen et al. have proposed to deposit catalyst using atomic layer deposition instead of PVD. The obtained CNT density on the atomic-layer-deposited catalyst approaches those found with physical-vapor-deposited catalysts [90]. Recently, they have applied arc plasma deposition to directly deposit nanoparticles with controlled size and density on a substrate [118]. However, this method is less accessible and much more expensive than the conventional PVD method.

In addition to the PVD method, catalysts could also be prepared via wet chemistry. Xiang et al. have proposed a spray coating process to prepare nanoparticles for the VA-CNT synthesis [122]. Compared with dip coating, where the amount of catalyst deposited is limited by the solubility of the precursor salt, spray coating methods set no limit on the amount of catalyst deposited, which is beneficial for the large-scale production. The resulting VA-CNTs from the spray coating reportedly have similar quality, crystallinity, tube diameters (1.85 to 1.35 nm) and carbon yield in comparison to dip-coating. The diameter of VA-CNTs could be tailored by changing the catalyst precursor solution.
2.2.3.3 Catalyst Support

The importance of the catalyst support is not to be underestimated. First of all, the catalyst support allows the formation of densely packed metal nanoparticles through their dewetting, owing to its low surface energy. Second, it prevents metal nanoparticles from coarsening excessively on the surface or inward diffusion into the bulk of the support, a phenomenon called sub-surface diffusion. Third, it also modifies the charge redistribution at the metal-oxide interface and the chemical interaction corresponding to atomic diffusion at the metal–oxide interface [36]. Interestingly, although a wide range of catalyst materials have been recognized as suitable for high quality and efficient growth of VA-CNTs, the number of commonly used supports is limited [123]. Therefore, catalyst support is a critical element in the CNT CVD and cannot be replaced easily. Thus far, VA-CNTs with highest density, growth efficiency and great yield are grown on an alumina support. Other oxides such as SiO₂ are also widely used.

For electronic applications, VA-CNTs directly grown on conductive substrate could be advantageous, as they provide robust mechanical, thermal and electrical contacts between the CNTs and the metal substrates. Compared with conventional methods, by which VA-CNTs are first grown on an alumina support and then transferred to a conductive substrate, direct growth avoids the time-consuming and delicate transfer process and provides superior electrical contact between CNT and substrate. However, unlike the oxide support, the metal substrate has a higher surface energy and could undergo complicated reactions and physical changes under the CVD conditions. In the past decade, steady progress has been made toward direct VA-CNT growth on a conductive substrate. Cartwright et al. have suggested that sp²-rich carbon mixture (85:15 sp²: sp³) could be used as a support for the VA-CNT growth [124]. This result could be useful for applications such as fuel cell electrodes and CNT-fiber composites. Esconjauregui et al. have compared the particle formation on substrate TiN and poly-crystalline PtSi films and observed homogenous nanoparticle distribution on PtSi, partly attributed to its low surface energy [125]. Zhong et al. have developed a Fe/Ti/Fe nanostructure on a SiO₂/Si wafer for the VA-CNT growth [126]. Later, the same group demonstrated the growth of single-walled VA-CNTs grown on commercially available Cu foil, with the help of a very thin alumina
layer (of 0.4 nm) [127]. The thin layer of alumina ensured the growth of SWCNT without damaging the Ohmic contact between SWCNT and the Cu support. The Fe sublayer prevents the catalyst diffusion into SiO$_2$/Si and thus minimizes the required thickness of the surface Fe layer. Later, Gao et al. have emphasized the importance of inhibiting catalyst sub-surface diffusion into the metallic substrate because of the higher diffusion coefficient of Fe in metal substrates than in oxide substrates [102]. In general, it is still challenging to grow VA-CNTs with tiny diameters and high density on a metal substrate rather than on an oxide support.

### 2.3 Controlled Synthesis of Graphene via CVD

#### 2.3.1 CVD by Carbon Precipitation on Transition Metals

The history of graphene growth on metals can be tracked back to more than half a century ago, with the first reports of monolayer and few layer graphite on Pt [128] and Ni [129]. At the time, the interpretation of the observed monolayers to be of a graphitic nature was not always immediate [130]. The lack of interest in graphene has limited further research for a few decades. It was not until 2004 when the mechanical exfoliation method by Novoselov et al. [13] nourished the exploration of graphene and its production, much to the surprise of fervent Mermin followers who believed that the isolation of monolayer materials at finite temperatures was unphysical because of inherent thermodynamic instabilities of their lattices [131, 132]. Thus, traditional methods based on direct growth were revived. Initial works in this period started with Ni-based growths [133] and continued by demonstrations on other metals. So far, graphene has been synthesized on polycrystalline Ni [70], Fe [134], Au [135], stainless steel [136], and single crystals of Ru (0001) [80], Ir (111) [78, 79], Rh (111) [137], Pt (111) [82], and Pd (111) [83]. Since these metals can dissolve a large amount of carbon in bulk, the growth mechanism roots mainly in precipitation with additional contributions from decomposition of the precursors on the metal surface. During cooling down the carbon from the bulk precipitates on the surface and forms the graphitic layers. Nevertheless, many of these catalysts including materials processing cost are quite expensive, as most of them are single crystalline metals of extremely high purity. Furthermore, controlling the number of
layers during the growth is also proved challenging. Nevertheless, conventional metallurgical approaches were adopted to achieve monolayer growth including rapid quenching and more exotic means of direct engineering of the catalyst, such as developing binary alloys \[138-140\]. Meanwhile, lattice mismatch between graphene and the catalyst metals (with the exception of Ni, with a mismatch of less than 1%) became an important hurdle. Lattice mismatch stimulates corrugation and wrinkle formation altering the intrinsic properties of graphene, such as the strain dependent work function, and producing Moire patterns \[141, 142\], often undesired for most purposes. Substrate interactions, in particular with Ru (0001) can also cause modifications in the electronic band structure \[81\]. So far, in this carbon precipitation method only polycrystalline Ni has been demonstrated to yield reasonable quality graphene (i.e., a charge mobility of 3,700 cm²V⁻¹s⁻¹) at low cost, scalable size, and low lattice mismatch \[70\]. However, it is extremely difficult to control the number of layers on polycrystalline Ni, which has different carbon saturation depending on the metallic grains, causing spatial variation of the graphene thickness. It is actually easier to grow monolayer graphene on Cu and transfer it three times to a triple-layer graphene stack than to precipitate exactly three layers of graphene on polycrystalline Ni. Therefore, even Ni has been surpassed by the controlled growths enabled by Cu. At present, Cu-based CVD is by far the most popular production method for large-scale graphene \[143\].

### 2.3.2 Surface mediated Graphene CVD on Cu

The practically zero carbon solubility of Cu \[144\] \((10^{-3}–10^{-2}\% \text{ for Cu at } 1000 \degree \text{C})\) makes it an ideal catalyst to synthesize graphene. Surface catalysis and the lack of bulk carbon cause the reaction to be self-terminating under particular growth conditions, yielding monolayer graphene \[84\]. Surface-based growth was experimentally evidenced by Li et al. using isotope-labeling of the carbon precursor during growth \[85\]. They showed that the graphene grows by attachment of the surface-adsorbed carbon to the edge resulting in a periodic, nested alternating isotope pattern (Figure 2.4a), which is distinct from the carbon precipitation from the bulk, which would have produced a random isotope spatial distribution (Figure 2.4b) \[85\]. Cu is also preferable for graphene transfer because it can be etched selectively.
and at low cost by chemicals, e.g., ammonium persulfate. Though it was extensively argued that the financial burden associated with the etching of the catalyst material dramatically increased the manufacturing cost, this issue has recently been circumnavigated with the advent of frame assisted bubble transfer [145], the reuse and purification of low-cost etchants like ferric chloride, and the recovery of Cu from the solution [146].

<table>
<thead>
<tr>
<th>Step</th>
<th>Method</th>
<th>Condition</th>
<th>Rational</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemical mechanical polishing</td>
<td>3.0-6.0 V 60 s in electropolishing solution</td>
<td>Reduce defects sites thereby eliminate nucleation density [147, 148]</td>
</tr>
<tr>
<td>2</td>
<td>Reduction</td>
<td>Acetic or hydrochloric acid pre-treatments</td>
<td>Remove surface oxide [149]</td>
</tr>
<tr>
<td>3</td>
<td>Annealing</td>
<td>900-1000 °C 15-30 mins for commercial 25 µm thick Cu foil</td>
<td>Yield larger Cu grains up to hundreds of µm [150, 151]</td>
</tr>
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</table>

Table 2.1 Cu substrate preparation procedure

A typical growth on Cu starts with conditioning of the substrate to reduce any native oxide (>500 °C or with plasma in reducing gas, such as H₂), high-temperature annealing to crystallize the Cu (i.e., 700 °C–1000 °C) then finally exposure to the hydrocarbon precursor (e.g., C₂H₂ [152], C₂H₄ [153], CH₄ [84], C₆H₆ [154], ....), solid [155] or liquid [156] at similar or lower temperatures. Graphene crystals then nucleate and enlarge with consuming the reactants formed by the catalysis of the carbon precursor on Cu. The available parametric window for continuous monolayer synthesis is wide [157]. For CH₄ growth temperatures can lie between 800 °C and 1050 °C, at chamber pressures of 0.01 mTorr to 760 Torr. However, the variation of the morphology by the growth parameters causes important variations in the physical properties of the deposited materials. In this section we describe the growth process in further detail and explain the fundamental mechanisms and kinetics that govern it. Flake morphology and secondary layers are also discussed.
Figure 2.4 Surface growth mechanism, adapted from ref. [85] and ref. [148]. (a, b) Micro-Raman characterization of isotope-labeled graphene monolayers grown on Cu (a) and Ni (b) foils. The integrated intensity of the G peak is shown, indicating spatially-alternating regions of C\textsubscript{12} and C\textsubscript{13} isotopes. (c) The schematics of the graphene nucleation, indicating the higher nucleation density at the scratch sites.

2.3.2.1 Substrate Preparation

Substrate preparation is a crucial step prior to graphene growth (Table 2). If the substrate surface is rough, an initial chemical mechanical polishing step is often necessary [147]. Scratches and defects on the substrate could function as nucleation sites during the synthesis (Figure 2.4c). Smoother substrates have less nucleation sites, thereby reducing the nucleation density and enlarging the attainable grain size [148]. However, excessive polishing may disturb the spatial uniformity of the graphene grain sizes. Although the nucleation sites are less dense compared with an unpolished surface, tiny defects on the polished surface can act as nucleation sites. It is these sparsely and inhomogeneously distributed defects that cause an inhomogeneous nucleation density and uneven grain size distribution. Consequently, the resulting monolayer film could have poor grain connectivity, high
sheet resistances, and perturbed and undulating surfaces owing to polishing [158].

The next preparation step is chemical reduction with often involving acetic or hydrochloric acid pretreatments [149]. A high-temperature annealing under pressures of 0.01 mTorr to 760 Torr, at 900 °C–1000 °C is the main furnace process to prepare the surface right before the growth step. Here, higher anneal pressures are known to smoothen the Cu surface [150]. This preparation process can take up to 30 min (for commercial 25-μm-thick foils). What is critical in this preparation step is the metallurgical composition of the Cu foil. Additional coatings or solvent impurities from the rolling manufacturing processes may cause nanometer-sized particles to form on the foils during graphene growth, which are visible under scanning electron microscope (secondary electron detection) [153, 158]. These small particles are difficult to remove and can remain attached to graphene even after transferring to other substrates.

Besides the composition, Cu crystallinity [159] and grain conformation have also been shown to be important for the catalytic process. Single or polycrystalline Cu can be used for graphene growth [160]. However, due to their low cost and wide availability, the most popular forms of Cu so far have been commercial foils and polycrystalline physical-vapor-deposited thin films. Larger grains are favorable, and the grain sizes of evaporation-deposited Cu films can be enlarged from tens of nanometers to a few micrometers by annealing at 900 °C–1000 °C [161]. This increase in the grain size can be more dramatic in Cu foils, with sizes increasing up to hundreds of micrometers.29a Crystalline orientation is also critical for the graphene growth [159]. Thermal annealing can recrystallize the catalysis-sensitive surface, yielding mostly monocrystalline orientation over the entire surface [153]. Electron back scattering diffraction (Figure 2.5a) shows that the annealing pretreatment renders the dominant surface orientation of Cu foils become (100); while for Cu films, annealing crystallizes the otherwise amorphous film to (111) surfaces[161]. Low-index Cu facets tend to yield higher areal densities of monolayer graphene with less defects (Figure 2.5b) [159]. On the other hand, Tao et al. has reported that Cu films can produce higher quality graphene compared to foils [161], where it is proposed that the higher H₂ content of the films may
replace the need for the gas-phase hydrogen and reduce the defect density.

![Figure 2.5](image)

**Figure. 2.5** Influence of the copper crystalline orientation, adapted from ref. [153] and [159]. (a) EBSD microscan of the Cu foil surface after high temperature anneal at 900 °C for 30 min. Inset: Inverse pole figure for the surface normal direction, showing the dominant copper crystallographic orientation is (100). (b) Intensity ratios $I_{2D}/I_G$ and $I_D/I_G$ for different Cu surface crystallographic orientations (the G' peak shown as 2D in the figure). Cu(111) has monolayer graphene, while others have multilayer coverage. Defect density appears to be independent of the surface orientation.

### 2.3.3 Transfer and Direct Growth on Insulators

Metal-catalyzed graphene may not be applied directly to the characterization of electronic, optical or mechanical properties or to the applications using these properties. For these applications and characterizations it is necessary to transfer the graphene onto various dielectric substrates, such as SiO$_2$ and HfO$_2$, or to lay it freestanding. On one hand, graphene is chemically inert against most of the common solvents and acids/bases even though it can be doped readily. On the other hand, it is possible to selectively remove the catalyst metal and the transfer media (i.e., polymer) to which graphene is attached. This selective removability is in part one of the main reasons for the success of the metal-catalytic CVD.

Whereas the polymer-mediated transfer process is easy, complications associated with wrinkle and crack formation as well as incomplete
cleanup of the residues from the transfer medium could all degrade the physical properties of the transferred graphene [162]. Hence, there have been recent attempts focusing on direct graphene synthesis on insulators, removing the need for any transfer. This section reviews common graphene transfer methods and discusses the various cleaning procedures employed. We conclude by summarizing advancements in direct growth on dielectric substrates.

2.3.3.1 Graphene Transfer

Early methods for graphene transfer from metal substrates have proven the possibility of relocating graphene by adhering it to a sub-micrometer-thick polymer layer [163]. A common wet transfer procedure begins with spin-coating of a polymer layer, e.g., poly methyl-methacrylate (PMMA), on the as-grown graphene/catalyst stack. The stack is then cured at 120-180 °C in the case of PMMA. Next, the catalyst metal (e.g., Cu) is etched away by use of aqueous etchant solutions such as FeCl$_3$ [164], Fe(NO$_3$)$_3$ [84], HCl [164], HNO$_3$ [165] and (NH$_4$)$_2$S$_2$O$_8$ [166, 167]at concentrations of 0.1-5 M. After etching Cu, the floating polymer/graphene stack is rinsed in water and “picked up” with a destination substrate and dried. Lastly, the polymer layer is removed by a proper etchant such as acetone. Improvements on this wet transfer scheme have been achieved over the past few years. For PMMA a secondary casting process has been introduced to release the strain after the initial polymer cure [168]. Groups have also recently abandoned pre-etch curing of polymer [167], which appears to encourage the PMMA/graphene to conform better to the destination dielectric substrate and so to reduce the detrimental wrinkling and cracks. Alternative methods for removing the graphene-PMMA from the solution have also been demonstrated such as picking-up of the film from above, slow lowering of the liquid level (Figure 2.6a), and reduced-angle fishing with a needle (Figure 2.6b) [167]. To retain the novel properties of the graphene, it is critical to ensure the graphene cleanliness during the transfer process. To achieve this goal, PMMA removal has been widely investigated. Heated acetone [169, 170], acetone vapor [171], and additional annealing [172] have been reported. At the moment acetone is being phased-out completely, being replaced by high temperature gas annealing, which will be discussed in detail in the following section. To exemplify the current
state-of-the-art transfer [167], optimal wet-transfer trend for centimeter-sized graphene starts by the spin-coating of PMMA (2% in anisole) at ca. 4000 rpm, continued with Cu etching by the (NH₄)₂S₂O₈ solution (ca. 0.1-0.5 M) in two steps (first step to remove the backside graphene), followed by an air drying (ca. 30 min) and a vacuum (ca. 3 hours) drying. Lastly, the PMMA layer is removed by annealing at 400°C under Ar and H₂ (e.g., 500 sccm : 500 sccm) flows for 2 hours.

Table 2.6 Graphene transfer methods. (a, b) Schematics for different removal methods to attach the graphene/PMMA layer onto the destination substrate. Heating at 180 °C for 30 min after drying facilitates the flattening of the PMMA layer on the destination substrate, adapted from ref. [167] (c) Schematics of the delamination method that peels graphene without etching Cu and its application to renewable transfer process, adapted from ref. [173] (d) A bubbling method to remove graphene/PMMA layer from Cu. Electrochemical reactions cause gas generation on the copper surface, which helps detach the graphene layer mechanically, adapted from ref. [174].

Other than the common wet-transfer technique as described above, numerous wet/dry methods have been demonstrated [175, 176].92b,99 For example, a direct transfer method exploiting the adhesion force of surface tension has been illustrated by sticking as-grown graphene to TEM grids [177]. Here a drop of isopropanol is placed on a TEM grid which stays on the Cu foil with graphene. During solvent evaporation, the surface tension draws the graphene from the Cu surface to the
amorphous carbon grid. Because this method has low yields, PMMA-based method is still preferred by many. Alternatively, a dry transfer technique based on poly dimethyl-siloxane (PDMS) can be used, albeit with less conformity [175]. All these methods share complete removal of polymer residues as the critical issue.

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Procedure</th>
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<tbody>
<tr>
<td>Wet transfer [168-172]</td>
<td>Polymer (PMMA) based, high yield</td>
<td>(1) Cu/graphene spin-coat polymer (2) cure in air at 120-180 °C (3) etch Cu (4) pick up graphene/polymer layer with desired substrate (5) remove PMMA with heated acetone, acetone vapor or annealing</td>
</tr>
<tr>
<td>Dry transfer [175]</td>
<td>PDMS based</td>
<td>(1) coat graphene/Cu with self-release layer (2) contact with elastomeric stamp (3) etch Cu (4) contact with target substrate (5) remove self-release layer</td>
</tr>
<tr>
<td>Direct transfer on TEM grid [177]</td>
<td>Low yield</td>
<td>(1) place a drop of isopropanol on TEM grid which stays on the Cu foil with graphene, (2) evaporate isopropanol, graphene draw from Cu foil towards amorphous TEM grid by surface tension</td>
</tr>
<tr>
<td>Etch-free transfer [173]</td>
<td>Epoxy based, reusable Cu</td>
<td>(1) precisely measure the graphene-Cu adhesion energy (2) chose an epoxy/substrate pair (3) remove graphene from its Cu catalyst without any etching</td>
</tr>
<tr>
<td>Bubble transfer [145, 146, 174]</td>
<td>Reusable Cu, minimized unintentional doping</td>
<td>(1) spin-coat PMMA (2) press Kapton tape on PMMA with a teflon roller (3) immerse in DI water at 90°C (4) press the stack on to target substrate for 40mins at 140°C (5) remove PMMA with acetone and RTA</td>
</tr>
<tr>
<td>Direct transfer via laminatio n [178]</td>
<td>Applicable to flexible substrates</td>
<td>(1) place graphene/Cu in between target substrate and protective paper (2) put the stack in between two PET films (3) insert into lamination machine (4) remove PET films and protective paper (5) etch Cu</td>
</tr>
</tbody>
</table>

Table 2.2 Summary of Graphene Transfer Methods.
Large area, mass scale transfer techniques include roll-to-roll processes comprising major steps of: (1) adhering graphene to various polymers which act as thermal, optical or chemical release layers; (2) etching of Cu and reattaching to the destination substrate; and (3) removal of the release layers [166]. More recently, renewable procedures to avoid the Cu etch step have been introduced. Figure 2.6c shows the delaminating method by Yoon et al. [173]. Here, a flexible substrate with an additional epoxy layer is adhered to the graphene. By precisely measuring the graphene-Cu adhesion energy (0.72 J/m²), coupled with an appropriate choice of the epoxy/substrate pair, they removed graphene from its Cu catalyst without any etching, with the aim of recycling the Cu for future growths. Another alternative method to retain Cu is so called a bubble transfer method (Figure 2.6d) [145, 146, 174]. Electrochemical reduction of water generates H₂ bubbles and detaches the graphene layer from the Cu foil grounded in a NaOH aqueous solution (0.25 M) or polarized at -5 V in a K₂S₂O₈ solution (0.05 M). However, this method still necessitates the use of a PMMA layer for mechanical integrity of the graphene layer. The procedures of several transfer methods are summarized in Table 2.2.

### 2.3.3.2 Transfer Cleanliness

So far no other wet or dry transfer method has surpassed the popularity of PMMA-based transfer, for almost all emerging methods have their own distinct drawbacks as described above. The PMMA-based transfer method is the most common for research purposes using centimeter-sized or larger area graphene, owing to its simplicity, high conformity, and compatibility with most of the destination substrates. However, PMMA and other polymer-based methods, often produce residues remaining on the graphene after transfer. While many organic solvents such as acetone efficiently dissolve the bulk PMMA, a thin layer (1-2 nm) often remains adsorbed. These residues could induce weak p-doping of the graphene [162]. A complicated wet-cleaning process based on the standard semiconductor cleaning recipes could improve residue removal.103 Nevertheless, presently the most efficient way to clean graphene is high temperature annealing. Lin et al. have characterized the removal of these residues by high temperature annealing [172]. A 200 °C anneal under H₂ removed most of the adsorbed polymer facing air, while retaining polymer (PMMA-G) and
some Cu particles in contact to graphene (Figure 2.7). Researchers have found out a way of removing the Cu remainder (or tiny precipitated particles) by replacing the common Cu etchant (FeCl₃), which creates poorly water-soluble Cu(I) chloride, with (NH₄)₂S₂O₈ that produces water-soluble Cu(II) chloride [179]. Unlike the Cu remainder, the removal strategy of PMMA-G is not yet satisfactory [180]. Use of an additional O₂ annealing may improve the result, through defect generation by partial oxidation of graphene is a concern. Graphene annealing in H₂ at higher temperatures such as 250 °C does not yield better cleaning, due to formation of covalent bonds between PMMA and graphene that already produce sp³ hybridization [172]. Nevertheless, there are reports about improved cleanliness at 400 °C annealing in H₂ [167, 181]. While some processes yield transfers of CVD graphene with almost similar quality to the mechanically exfoliated graphene, strong needs for better transfer and cleaning methods are calling for immediate attention.

Figure 2.7 Transfer cleanliness. (a-c) TEM images of graphene after PMMA-based wet transfer and two step annealing under air and H₂/Ar flows at 200 °C for 2 hours. (d) Schema representing Cu remaining, PMMA facing air (PMMMA-A) and graphene (PMMA-G). (e, f) Same TEM images as (b, c) with color coding showing the residues as indicated by the schematic in (d), as adapted from ref. [172].

2.3.3.3 Direct Growth on Dielectrics

Direct synthesis of graphene on insulating substrates is the ultimate solution to avoid transfer and its associated problems described above.
Several studies have demonstrated graphene-like film deposition on SiO$_2$ [182-184], quartz [185], sapphire [186-188], boron nitride [189], mica [190], and MgO [191]. Early work by Ismach et al. has showed that growth on thin-film Cu on quartz, followed by the sublimation of the Cu layer, left the graphene on the quartz substrate (Figure 2.8a) [185]. However, the continuity and the quality of the resulting graphene were low with particular regard to film wrinkling. Alternatively, thin film Cu or Ni on insulating substrates can be used as a medium through which to diffuse and catalyze carbon reactants for forming graphene at the interface between the metal catalyst and the substrate [182, 183]. Su et al. have reported a moderate charge mobility of graphene (670 cm$^2$V$^{-1}$s$^{-1}$) from this method (Figure 2.8b) [182]. This method is promising but still requires metal removal after the growth. To avoid this etch step, a remote catalysis method has been demonstrated [192]. CH$_4$ is first flown over a Cu foil placed upstream in a tube furnace, which catalyzes CH$_4$ dissociation at 1000 °C. Next, the active carbon species are desorbed from the Cu surface, in part along with the subliming Cu. These species then deposit onto the destination substrate while flowing downstream where graphene is grown, yielding mobilities around 100-600 cm$^2$V$^{-1}$s$^{-1}$.

The most promising way of graphene synthesis on insulators is a metal-free growth. Hwang et al. in 2010 demonstrated C$_3$H$_8$-based CVD of graphene on sapphire (0001) at temperatures above 1350 °C.109b Later a lower temperature growth was achieved by employing alcohol as the carbon source, albeit giving inferior electronic quality.109c More recently, a high charge mobility of 3000 cm$^2$V$^{-1}$s$^{-1}$ has been demonstrated by Fanton et al. by using a CH$_4$-based CVD on sapphire at 1550 °C (Figure 2.8c) [186]. High growth temperatures could be a drawback, for they limit the available range of substrates. Molecular beam epitaxy from pure carbon filaments can be used on biotite mica (001) surfaces heated to 500-1000 °C [190]. Furthermore, MgO-based substrates can support graphene growth at even lower temperatures of 325 °C using C$_2$H$_4$ [191]. With limited choice of substrate and temperature, direct CVD on insulators remains to be much improved before thus produced graphene reaches the quality comparable to graphene produced by Cu-based CVD methods.
2.3.3.4 Electronic Properties of CVD-synthesized Graphene

Charge mobility and sheet resistance are two of the most common indicators of the electronic quality of graphene. While the highest mobility values have been reported for mechanically exfoliated graphene, CVD-based graphene is becoming comparable, having room temperature mobilities exceeding several thousand cm\(^2\)V\(^{-1}\)s\(^{-1}\) [72, 150]. On the other hand, in order to utilize graphene as transparent conductors, sheet resistances less than 10 \(\Omega/\text{sq}\) is required [193]. Thus far this requirement over large areas has been difficult to reach, with most reported values ranging between 100 and 1000 \(\Omega/\text{sq}\). This section introduces the growth-related factors that define the mobility and sheet resistance values for CVD-grown graphene.

Grain boundaries and connectivity are critical in defining the resistance associated with boundary scattering by distorted
crystallinity. Huang et al. have reported an inter-grain resistivity of 60 Ω-μm, corresponding to roughly one third of the resistance introduced by the grains (ca. 250 nm in diameter) [164]. However, inter-grain resistivity is highly dependent on the growth conditions. Figure 2.9a-c show the boundary conductivities for graphene grown in fast and slow growth regimes, yielding approximately 1 μm and 50 μm in grain sizes. Contrary to the expectation, the smaller grain graphene presents better grain connectivity by an order of magnitude. However, for large domains (more than 10 μm) the larger grain graphene showed a slightly more conductive film (Figure 2.9d). Furthermore, overlapping regions (i.e., at a thickness of 325 nm) for the larger grain graphene can improve the boundary conductivity by around 45% [73].

**Figure 2.9** Charge mobility and graphene domains. (a, b) False-color TEM images of graphene with different domain sizes (scale bars: 1μm). (c) Conductivity of the grain boundaries with respect to the charge carrier density, indicating the grain connectivity for small domains is electronically better than the connectivity of larger-domains. (d) Resistance with respect to channel length. For short channels small grains have better conductivity, while for distances above 10 times the smaller-
domain size large-domain graphene becomes more conductive due to less number of boundaries, adapted from ref. [73].

While overlapping crystals may be beneficial to enhance inter-grain connectivity, wrinkles and ripples are unquestionably detrimental to the conductivity. Zhu et al. have calculated that ripple heights of up to 6 nm may occur during folding, resulting in boundary resistivity values of the order of 200 Ω-μm regardless of the width of the fold [194]. Here, diffusive transport and interlayer charge tunneling could increase resistivity. Nanometer-scale ripples can also add considerable resistances. A report by Ni et al. has claimed that increasingly perturbed Cu topographies can cause the formation of quasi-periodic nano-ripples [195]. These ripples can then act as sources for flexural phonon scattering, which limits the minimum monolayer sheet resistance to 80 Ω/sq for a carrier density of 1012 cm⁻². To avoid these ripples strain engineering can be employed [196], or alternatively doping can increase the charge carrier density with enhancing the conductivity without the need of strain engineering [193]. In contrast to intentional graphene doping to minimize the sheet resistance, substrate induced doping could be detrimental. A careful selection or treatment of the substrate with self-assembled monolayers may be one possible bypassing route. So far, boron nitride [197] and self-assembled monolayer dielectrics have been demonstrated for effective passivation of SiO₂ substrates [198].

2.3.3.5 Scaling-up Schemes

Presently meter-scale production of graphene can only be possible by two methods: CVD growth and liquid-phase exfoliation. The latter can be ruled out for applications requiring higher electronic conductivity/mobility because of low flake concentrations (on the order of 0.1 mg/ml) [199], very low truly monolayer flake yields (on the order of 1%) [200], and most importantly, the inherent difficulties in achieving continuous monolayers. Hence, CVD, in particular the Cu-based growth, is most probably the only promising and viable method for scaling up the graphene synthesis currently.
Initial reports on large-scale graphene growth have been based on growths on Cu foils inside large-diameter tube furnaces, with foils up to 20 cm having been demonstrated coupled with roll-to-roll transfer processes for coating plastic substrates [166]. Later, a small roll-to-roll system has been fitted into a 25-mm-diameter quartz tube to produce low quality graphene on a narrow but continuous Cu foil [202]. Yamada et al. have employed a more advanced rolling system in a microwave plasma oven to obtain graphene, albeit with low crystallinity (at a width of 294 mm) at temperatures below 400 °C and with rather high sheet resistances of 10k-700 Ω/sq, which is perhaps well-suited for flexible transparent conductor applications [203]. An increasingly advanced roll-to-roll system was reported by Kobayashi et al. [77]. Here a 100-m-long sheet of graphene, with a charge mobility of 900 cm²V⁻¹s⁻¹, has been grown and transferred onto flexible plastic substrates by a series of roll-to-roll processes, as shown in Figure 2.10a-c. Meanwhile, Tao et al. have demonstrated better quality graphene, uniform over a 150 mm wafer, with Raman G’ peak widths of 25-35 cm⁻¹ and a charge mobility of 4,900 cm²V⁻¹s⁻¹ (Figure 2.10d-e) [201]. They employed a Cu thin film on a SiO₂/Si wafers which restricted the rolling process but enhanced the material quality [161].
Work is still ongoing throughout the industry to improve the quality and scalability of roll-to-roll and large-scale wafer-based CVD growth schemes.

2.4 Conclusion

Catalytic CVD has become the most convenient and popular synthesis method to produce high quality VA-CNTs and graphene. The properties of both materials grown by CVD strongly depend on the pretreatment and synthesis condition and the catalyst design. For the growth of VA-CNTs, a typical as-deposited Fe catalyst thin film undergoes a dynamic reconstruction on alumina support to form densely packed nanoparticles. The pretreatment condition and catalyst-support interaction determines the morphology of formed nanoparticles. Synthesis condition decides the nucleation density of CNTs on nanoparticles, self-organizing of CNTs into aligned structure and the growth termination (lifetime of catalyst) of VA-CNTs. Direct synthesis of VA-CNTs on conductive support is still in its infancy, and significant progress is needed for it to outperform the current Fe-alumina based synthesis protocols. For the growth of graphene, Cu offers self-limiting growth of a monolayer graphene with low wrinkling and rippling, due to its ultra-low carbon solubility. Advances in the understanding of the fundamental growth mechanisms have permitted the synthesis of high quality polycrystalline graphene with larger and better-connected grains. Meanwhile, optimization of the transfer and cleaning procedures has resulted in graphene with charge mobility close to that of mechanically-exfoliated counterpart, at scalable dimensions. Direct deposition of the monolayer graphene on insulating substrates promises the ultimate progress in the cleanliness and electronic exploitation of graphene, removing the necessity of using sacrificial metals and transfer processes. However, direct deposition remains challenging. Mass production of the monolayer graphene is likely to be realized in the near future by roll-to-roll processes handling meters-long Cu foils as the growth medium and flexible plastics as the destination substrate. In short, the growth of VA-CNTs and graphene by CVD have been discussed extensively in many aspects. Despite the great research effort in CVD synthesis of VA-CNTs and graphene, a few critical properties of the material could not yet been fully controlled, for example, the precise diameter control of
single-walled VA-CNTs and the layer control of graphene. In prospect, more quantitative models of the growth mechanisms of VA-CNTs and graphene would be very useful for orienting experimental works and assisting the analysis of experimental data.
3 VA-CNT Growth Kinetics and Fundamental Mechanisms

Parts of this chapter have been submitted for publication in:


3.1 Abstract

Gas-phase reactions among carbon precursors could have a significant effect on the catalytic synthesis of vertically aligned (VA-) carbon nanotubes (CNTs). State-of-the-art adjustment of the gas-phase reaction conditions is done ad hoc with low reproducibility, ascribed partly to an incomplete understanding of the mechanism how the gas-phase reaction influences the growth kinetics of VA-CNTs. Here, we investigate this mechanism and demonstrate that in the presence of prominent gas-phase reaction, the growth kinetics characterization shifts from a single rate-limiting reaction to a multi-route reaction with each pathway having its own rate-limiting step. The rate of the gas-phase reaction could be tailored by the partial pressure and thermal history of a carbon feedstock (e.g., acetylene). According to in-situ mass spectrometry and numerical simulation, a rich set of secondary pyrolysis products (e.g., C₄H₄ and C₆H₆) are found to be produced in the gas phase and carried to the catalyst surface. We propose that the secondary pyrolysis products yield CNTs through alternative reaction pathways, promoting the overall growth rate of VA-CNTs. Our findings further the current understanding of the VA-CNT growth from thermally rearranged precursors, instrumental to applications such as diameter-controlled growth and CMOS-compatible low-temperature growth.
3.2 Introduction

Chemical vapor deposition (CVD) growth of vertically aligned carbon nanotubes (VA-CNTs) has garnered great interest because of its scalability [204], low-cost, and high production yield. Despite the effort in the CVD of VA-CNTs in the past decades, the fundamental mechanism of the CNT growth is still not well understood, leading to low reproducibility and controllability [205]. Previous studies have thus far suggested a sequential process of four steps: (i) mass transport and reaction in the gas phase [206-208], (ii) surface reactions on the catalyst, (iii) carbon diffusion on the catalyst particle surface [209] or through bulk [210], and (iv) carbon incorporation into CNTs. While the other steps have been extensively investigated, active discussions on the aspect of the gas-phase reactions and its impact on the growth result are rare.

Due to the transport time from a gas inlet to a catalyst substrate, a CVD process unavoidably involves thermal rearrangement of feedstock gases. During this step, common feedstock gases such as C\(_2\)H\(_2\) (acetylene) and C\(_2\)H\(_4\) (ethylene) can generate a combination of secondary species [211], which influences VA-CNT growth rate and quality [199, 212-214]. The more reactive the gases and the chamber conditions, the more thermally rearranged the precursor gases. The extent of the gas-phase reactions depends primarily on gas pretreatment temperature, gas dwell time [215], and gas composition [216]. We have previously proposed TG-CVD, which can effectively modulate the gas pyrolysis for a C\(_2\)H\(_2\)-based CVD. In particular, by introducing a linearly decreasing temperature gradient from the gas inlet to the catalyst substrate, TG-CVD can condition the optimal gas-phase reaction environment for an efficient and high-quality CNT growth [217].

Several studies have shown the significant impacts of gas-phase pyrolysis products on the rearrangement of carbon precursors and subsequently the CNT growth. Meshot et al. have decoupled CVD temperature into catalyst substrate temperature and gas pre-treatment temperature to observe that the substrate temperature determines CNT diameter, whereas that the thermal treatment generates a wide range of hydrocarbon species that either promote or inhibit the CNT growth [212]. Yasuda et al. have introduced thermal history (dwell
time) of feedstock gases as one of the CVD parameters with which to report a strong correlation between the gas dwell time and various aspects of the growth results (e.g., conversion rate of carbon source to CNTs) [215]. Nessim et al. have observed a transition of the CNT crystallinity, from rather amorphous to single crystalline, under different thermal pre-treatment conditions of precursor gases [91]. Moreover, Matsumoto et al. have observed that the pyrolysis of C$_2$H$_2$ could strongly influence the growth efficiency of single-walled CNTs [218]. These works provide a hint that some of these gas pyrolysis products are likely important reactants for the CNT production, while others could be detrimental to the growth efficiency and quality control. The subsequent work by Plata et al. has identified the alkyne types of the pyrolysis products (i.e., C$_2$H$_2$, C$_2$HCH$_3$ (methyl acetylene), and C$_4$H$_4$ (vinyl acetylene)) as important precursors while excluding the previously suspected species such as C$_6$H$_6$ and CH$_4$ [216]. Ma et al. have later found out that at CVD temperatures for the CNT growth, C$_2$H$_2$ polymerizes into unsaturated carbon chains, mainly comprising C$_4$H$_4$ [214]. Although a number of theoretical and experimental observations have shown the potential influence of gas-phase reactions on the CNT growth, the underlying mechanism of VA-CNTs in the presence of prominent gas-phase reactions remains still to be elucidated.

Here, we investigate systematically the influence of gas-phase reactions on the VA-CNT growth by varying the ratio of the secondary carbonaceous precursors to initial acetylene using TG-CVD. Temperature gradients were applied between the gas inlet and the catalyst substrate in the cold-wall CVD reactor. We observed extra growth rate enhancement for high C$_2$H$_2$ partial pressure, high gas pre-treatment temperatures, and long dwell time. In the presence of a thermal zone for active precursor rearrangement, the apparent activation energy of VA-CNTs deviates from its value for no such rearrangement as the C$_2$H$_2$ partial pressure varies. The deviation of the activation energy indicates an alteration of the growth mechanism. Based on these findings, we propose a mechanism of the gas-phase-assisted growth with a model by taking multiple parallel reaction pathways into account.
3.3 Experimental Methods

3.3.1 Temperature Gradient CVD

CNT growth experiments were performed in a vertical, cold-wall CVD reactor (Black Magic ProTM, Aixtron AG) with dual heaters. In this reactor, a gas mixture injected downward from a top shower head impinges on a sample stage 41 mm below. While passing the reactor chamber, the gas mixture undergoes a pre-defined temperature gradient, a characteristic of TG-CVD. Dual heaters, one (top heater) placed next to the shower head and the other (bottom heater) right beneath the sample stage, are employed to determine and control thermal boundary conditions for the temperature gradient inside of the chamber. Two boundary temperatures at the gas shower head and at the sample stage are measured by a thermocouple and an infrared pyrometer, respectively. The infrared radiation pyrometer has accuracy of ± 6 °C and can measure the sample stage temperature using a two-wavelength ratio method. A detailed description of the TG-CVD system could be found in [217].

We separate our growth conditions into two categories: top heating (TH) mode and bottom heating (BH) mode. In a TH mode, the top heater is used as the main heat source creating a negative temperature gradient toward the catalyst substrate, whereas in a BH mode, the bottom heater is used as a main heat source generating a positive temperature gradient toward the catalyst substrate. Therefore, in the BH mode, the precursor gas flows through thermal zones cooler than the catalyst before reacting with it. In the TH mode, the gas passes through thermal zones hotter than the catalyst that is indirectly heated by the top heater via thermal radiation.

In order to analyze the gas mixture composition from the thermal treatment of the gas precursor, we collected mass spectra in situ by a quadrupole mass-spectrometer residual-gas analyzer (Vision 2000-C/Microvision 2, MKS), demonstrating relative changes in the abundance of selected compounds. The mass spectrometer probe is directly inserted into the CVD chamber 5-8 mm above the catalyst substrate to detect the gas composition direct above the catalysts.
3.3.2 Catalyst Preparation and CNT Growth

All CNTs are grown on the same catalyst, consisting of 2 nm Fe atop of 20 nm Al2O3 deposited on a Si substrate by e-beam evaporation (Univex 500, Leybold). Here, we chose 585-700 °C as the parametric window for the catalyst substrate temperature, while fixing the temperature difference between top heater and catalyst substrate to be -160 °C for TH mode and 200 °C for BH mode for all experiments. Before the growth, the chamber was thermally cleaned under pure H2 at 800 ºC for 10 min. Then, the catalyst substrate were loaded onto to the sample stage, followed by chamber evacuation to sub-0.2 mbar. At a ramp rate of 300 ºC/min, the catalyst substrates were first raised to 700 ºC by the bottom heater and maintained at that temperature for catalyst reduction for 300 s, with the total chamber pressure maintained at 10 mbar. A feed gas mixture included 400 sccm of H2 and 600 sccm of Ar. We applied identical heating and feed gas conditions in this pre-treatment process for all of our experiments to ensure the constant initial activity of catalyst. After catalyst pre-treatment, a quick thermal rearrangement was introduced under pure Ar. By changing the top and bottom heater temperatures, desired temperature gradient was developed in this period. During the CNT growth, C2H2 (5, 15 or 25 sccm) was injected into the chamber along with constant amounts of H2 (200 sccm) and Ar (300 sccm). The total pressure during the growth was kept at 480 mbar (± 0.2 mbar). The initial growth rate was obtained by averaging the VA-CNT heights of the initial 100-s-long growths.

3.3.3 Reacting Flow Simulation

In order to resolve the gas composition impinging on the catalyst substrate during TGCVD, we simulated a reacting flow of 199 reactions and 56 gas species based on a Chemkin reaction library [219] using a stagnation flow model. The CVD chamber was modelled as a one-dimensional system, based on a kinetic model of laminar premixed C2H2 and C2H4 flames [220] with excluding the oxygen-containing reactions. In this simulation, we neglected an influence of moisture or any O2 source from the environment on unwanted contamination of the reaction chamber. The boundary conditions were as follows: at the shower head, the mole fractions of the reactants were imposed (C2H2:
0.0099, H₂: 0.3960, Ar: 0.5941); the bulk axial velocity at the inlet was
given based on the shower head flow area and the volume flow rate of
the incoming mixture calculated from the given top heater temperature
and chamber total pressure (480 mbar); the substrate that holds the
catalyst piece was assumed to be non-reactive and impermeable.

3.4 Results and Discussions

3.4.1 Apparent Activation Energy

It is known that C₂H₂-containing feedstock gases generate a wide
varieties of secondary species via pyrolysis [217]. Various types and
compositions of the carbonaceous species would eventually approach
the catalyst and participate in the subsequent surface catalytic
reactions, precipitating carbon products such as CNTs. For a given
catalyst temperature (T_cat), gas precursors in the TH mode experience
much higher temperatures than in the BH mode during their travel to
the catalyst, and therefore vigorous thermal rearrangement would
occur to the precursors in the TH mode. Distinct thermal histories of
C₂H₂ can result in different active reactant species atop the catalyst and
hence influence the growth kinetics of VA-CNTs.

![Figure 3.1](image-url) Activation energy of the CNT growth for various heating modes and
C₂H₂ partial pressures. (a) Different P_C₂H₂ associate with different
apparent activation energies (Eₐ) in the top heating (TH) mode (blue for
1 mbar, red for 3 mbar and green for 5 mbar of C₂H₂). The denoted
temperature for Arrhenius plots are the catalyst temperature, T_cat. (b) Eₐ
is observed to be independent of $P_{C_2H_2}$ in the bottom heating (BH) mode, based on both data from our study and others [210], whereas it clearly depends on $P_{C_2H_2}$ in the TH mode.

In order to verify this hypothesis, we collected the initial growth rates of VA-CNTs in the two heating modes at various $C_2H_2$ partial pressures ($P_{C_2H_2}$). Acquisition of such kinetics data allows the comparison among different heating modes in detail by drawing Arrhenius plots accurately and determining the activation energy of each heating mode. We varied $P_{C_2H_2}$ in the range of 1-5 mbar. In the TH mode, we observed a change of the apparent activation energy, $E_A$, of the VA-CNT growth with respect to $P_{C_2H_2}$: $E_A = 1.18$ eV at $P_{C_2H_2} = 1$ mbar and increases to 1.37 and 1.51 eV at $P_{C_2H_2} = 3$ mbar and 5 mbar, respectively (Figure 3.1a). In contrast, no such dependency of apparent $E_A$ on $P_{C_2H_2}$ was observed in the BH mode (Figure 3.1b, black lines); our CNT growth data in the BH mode shows $E_A$ with a constant value of $1.42 \pm 0.01$ eV as $P_{C_2H_2}$ triples. Wirth et al. have also reported a constant $E_A$ independent of $P_{C_2H_2}$, in the BH mode and under the isothermal conditions, indicating an invariant rate-limiting mechanism [210]. Under the assumption of bulk-diffusion-limited growth, a constant $E_A$ around 1-1.7 eV is expected. However, the bulk-diffusion-limiting mechanism is insufficient to explain the $P_{C_2H_2}$ dependency of the apparent $E_A$. Such a dependency of $E_A$ indicates an out-of-proportion increase of the growth rate with $P_{C_2H_2}$ in the TH mode, in which gas thermal rearrangement is enhanced.

We postulate that the gas-phase reaction of $C_2H_2$ may introduce a cumulative impact on the growth kinetics of VA-CNTs by altering the composition and concentration of actual gaseous reactants. In the BH mode, the gas-phase reaction is suppressed by low temperatures of the pre-treatment gas thermal zone; consequently, the cumulative effect of the gas-phase reactions is eliminated, manifested by a constant $E_A$. 
3.4.2 Gas-Phase Reaction

To support our postulation that the products of the gas-phase reaction of \( \text{C}_2\text{H}_2 \) influences the CNT growth kinetics, we first measure the gas-phase composition directly above the catalyst substrate by in-situ mass spectrometry (Fig. 2). This measurement reveals that a wide range of gas species are actually arriving at the catalyst. Among them, we selected 6 mass-to-charge (m/z) ratio values (i.e., 16, 26, 28, 40, 52, 78) to monitor \( \text{CH}_4 \), \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \), \( \text{Ar} \), \( \text{C}_4\text{H}_4 \), and \( \text{C}_6\text{H}_6 \), respectively. \( \text{C}_4\text{H}_4 \) and \( \text{C}_6\text{H}_6 \) are supposed to be the most dominant products of thermal \( \text{C}_2\text{H}_2 \) polymerization [219, 221]. \( \text{Ar} \) as a carrier gas maintains the constant flow rate and partial pressure and is employed to normalize the other species and calculate the relative abundance.

**Figure 3.2** In-situ mass spectra collected by a mass spectrometer (MS) gas analyser, demonstrating relative abundance of selected mass-to-charge (m/z) ratios. The m/z values of interest are related to \( \text{CH}_4 \) (16), \( \text{C}_2\text{H}_2 \) (26), \( \text{C}_2\text{H}_4 \) (28), \( \text{Ar} \) (40), \( \text{C}_4\text{H}_4 \) (52) and \( \text{C}_6\text{H}_6 \) (78). Two representative \( T_{\text{cat}} \) of 600 °C (a) and 750 °C (b) are compared. BH mode at \( P_{\text{C}_2\text{H}_2} = 3 \text{ mbar} \), TH mode at \( P_{\text{C}_2\text{H}_2} = 3 \text{ mbar} \), and TH mode at \( P_{\text{C}_2\text{H}_2} = 1 \text{ mbar} \) are marked in cyan, red, and dark red, respectively.

First, we compare the gas compositions and concentrations in the BH and TH modes for a fixed \( P_{\text{C}_2\text{H}_2} \). At \( T_{\text{cat}} \) of 600 °C and \( P_{\text{C}_2\text{H}_2} \) of 3 mbar, the relative abundance of the pyrolysis products - especially \( \text{C}_4\text{H}_4 \) and \( \text{C}_6\text{H}_6 \) (m/z 52 and 78) - is much higher in the TH mode (Figure 3.2,
red) than in the BH mode (Figure 3.2, blue). When $T_{\text{cat}}$ is increased to 750 °C, we observe a similar tendency of more pyrolysis products in the TH mode than in the BH mode with all the partial pressures of the pyrolysis products increased by at least half an order of magnitude (Figure 3.2b). Next, we varied $P_{C_2H_2}$ in the TH mode. When $P_{C_2H_2}$ is decreased from 3 mbar to 1 mbar at a fixed $T_{\text{cat}}$ of 600 °C, the relative abundance of $C_4H_4$ decreases by about an order of magnitude, and that of $C_6H_6$ drops below $10^{-6}$ (Figure 3.2a, red vs dark red). The $P_{C_2H_2}$ reduction at $T_{\text{cat}}$ of 750 °C also decreases the abundance of pyrolysis products including $C_4H_4$ and $C_6H_6$. In other words, an increase of $P_{C_2H_2}$ in the TH mode results in out-of-proportion elevation in the abundance of pyrolysis products. Finally, we compare the gas pyrolysis at different $T_{\text{cat}}$ while fixing $P_{C_2H_2}$ and heating mode (Figure 3.2a vs 3.2b). For all $P_{C_2H_2}$ and heating modes (BH and TH), higher partial pressures of the pyrolysis products are observed in 750 °C than in 600 °C, explainable by an overall increase in the average pyrolysis temperature. In general, heating mode, $P_{C_2H_2}$ and $T_{\text{cat}}$ can all influence the carbon precursor to vary the active carbonaceous reactant species atop the catalyst.

![Figure 3.3](image)

**Figure 3.3** Chemkin-based reacting flow simulation results. (a) Simulated partial pressure of major pyrolysis products approaching catalyst substrate (e.g., $C_2H_4$, $C_3H_4$, $CH_4$, $C_3H_4$ and $C_6H_6$) as a function of the substrate temperature. (b) Contour plot of the predicted $C_4H_4$ partial pressure over the catalyst substrate as a function of the gas inlet $P_{C_2H_2}$ and the substrate temperature.
To analyse the gas-phase reaction in TG-CVD in a more comprehensive way, we compared the in-situ mass spectrometry result with a reacting flow simulation based on our chamber configuration and CVD conditions (see section 3.3.3). According to the simulation, the major pyrolysis products appear to be polymerized building blocks ($C_3$ and $C_4$ species), decomposition fragments ($C_1$ and $C_2$ species), $C_2H_4$, unreacted $C_2H_2$, and $H_2$. The partial pressures of the feedstock ($C_2H_2$), reductant ($H_2$) and the carrier gas (Ar) are relatively constant due to their significantly high initial concentrations. Other carbonaceous species, such as $C_2$ species (ethane, $C_2H_6$; ethylene, $C_2H_4$; vinyl radical, $C_2H_3$; and the other $C_2$ intermediates), $C_3$ species (propene, $C_3H_6$; propadiene, $C_3H_4$; propyne, $C_3H_2$), $C_4$ species (vinyl acetylene, $C_4H_4$; butene, $C_4H_8$; butadiene, $C_4H_6$; butadiene radical, $C_4H_2$; and the other $C_4$ species) and benzene, change their partial pressures (mole fractions) drastically over a few orders of magnitude (Figure 3.3a). Noticeably, $P_{C_4H_4}$ changes over three orders of magnitude from $10^{-6}$ to $10^{-3}$ bar depending on temperature and initial $P_{C_2H_2}$ (Figure 3.3b).

$C_4H_4$ has been recognized a key species to enhance the growth efficiency and quality of VA-CNT [214]. The structure of $C_4H_4$ with two $sp^2$-hybridized carbon bond can be easily assembled to a CNT building block. Moreover, $C_4H_4$ contains a triple bond that can be easily opened for surface catalytic reactions. Although benzene shares the similar structural advantage, the high thermal stability of benzene prevents it from actively partaking in the CNT synthesis.

3.4.3 Generalized Reaction Kinetic Formulation of the VA-CNT Growth

The secondary pyrolysis products have distinctive properties (e.g., structures, activities in catalytic reactions, etc.) and could participate in the surface catalytic reaction of the CNT growth through their own reaction pathways (Figure 3.4a). In the absence of gas-phase reactions, $C_2H_2$ arrives at the catalyst to dehydrogenate and dissociate into carbon monomers and yield CNT through bulk or surface diffusion (Figure 3.4a, left) [222]. In the presence of a prominent gas-phase reaction, $C_2H_2$ undergoes thermal pyrolysis to generate secondary species, largely comprising $C_4H_4$ [214]. Each of these species participates in individual catalytic surface reactions and diffusion
pathways to incorporate into VA-CNT (Figure 3.4a, right). C₂H₂ is known to bond very easily and strongly to a transition metal surface due to its strong interaction with the d-orbital, which leads to the exchange of electrons between the d-orbitals and the antibonding orbitals of adsorbed C₂H₂ [223, 224]. In the range of P_C₂H₂ applied in this study, the surface sites can be considered as a layer of adsorbed C species as a carbon reservoir in equilibrium comprised of molecules of C₂ species and their derivatives [225].

Molecules of C₂ species adsorbed on Fe particle can either dissociate into two atomic carbons or a dimer, each possibility resulting in its individual reaction pathway (Figure 3.4b). Through one pathway, C₂ molecules first dissociate into single C atoms and then diffuse through the bulk catalyst particle (Figure 3.4b, Path 1). Atomic carbons are prone to diffusion in the bulk catalyst rather than on the surface due to a large surface-to-volume ratio of catalyst particles [226]. In addition, adsorbed C₂ dimers could bypass the dissociation step and incorporate directly into CNT through surface diffusion. Surface-diffusion-limited growth has Eₐ around 0.4 eV and are often observed in a plasma-enhanced CVD [209, 227, 228]. However, the observed apparent Eₐ in our study is much higher than surface diffusion Eₐ and lies in the regime of bulk diffusion Eₐ, thus we only consider bulk diffusion limited reaction pathway.

Alternatively, the adsorbed C₂-species molecules can interact with the impinging gas species directly and undergo a polymerization-like reaction to construct CNTs [229]. In the transition metal catalysis, the cyclotrimerization of alkynes that combines three acetylene molecules into a hexagonal building block has been known for decades. We consider a simplified reaction mechanism based on carbon mass conservation. C₄H₄, including their derivatives, are referred to as C₄ species groups, respectively. We assume that gas molecules can impinge and react directly with an adsorbed species on the catalyst site through capture, isomerization, and insertion, as in the Eley-Rideal reaction, often used to describe the selective C₂H₂ hydrogenation on the transition metal like Fe [230, 231]. As a result, C₄ and other secondary species from the reactant gas mixture could possibly react with the adsorbed C₂ species via the Eley-Rideal mechanism and subsequently diffuse on the surface to participate in the CNT formation (Figure 3.4b, Path 2 in blue; also other pathways in green). Due to the
nature of the Eley-Rideal mechanism, the reaction rate depends not only on the catalyst active site density but also on the impinging frequency of gaseous C\(_4\) species.

Through the above pathways, various forms of carbonaceous precursors contribute to the CNT growth. Each pathway contains a series of reactions with a distinct rate-limiting step, represented as follows:

\[ v_1 = \sigma_s A_1 e^{-E_{A1}/k_B T}, \]  
\[ v_2 = \sigma_s [C_{C_4}] A_2 e^{-E_{A2}/k_B T}, \]

where, two typical pathways are listed, namely, the diffusion limited pathway (Fig. 4a left and Fig. 4b, denoted as pathway 1) and a polymerization-like reaction pathway in the Eley-Rideal mechanism (Figure 3.4a right and Figure 3.4b Path 2). \( v \) is the reaction rate of the rate-limiting step in pathways 1 and 2; \( A_1 \) and \( A_2 \) are the pre-exponential factors; \( \sigma_s \) is the areal density of the active catalyst sites; \( E_A \) is the activation energy of the rate-limiting step; \( C_{C2} \) and \( C_{C4} \) are the impinging concentration of gaseous C\(_2\) and C\(_4\) species, respectively. We assign \( E_{A1} = 1.5 \text{ eV} \) and \( E_{A2} = 1.25 \text{ eV} \) by referring to the literature [110, 209, 232-234]. Concentration of the gaseous C\(_4\) species could be deduced from the result of the aforementioned 1D reacting flow simulation by

\[ [C_{C_4}] = [C_{C_2}] A_{C_4} e^{-E_{AC_4}/k_B T}, \]

which associates \([C_{C_2}]\) with the rate of the reaction pathway 2. We extracted apparent activation energies \( (E_{AC_4}) \) and their pre-exponential factors \( (A_{C_4}) \) for various C\(_2\)H\(_2\) partial pressures \( ([C_{C_2}] \)). Combing eq. (3.1) and eq. (3.2), the overall reaction rate as a sum of these pathways can be expressed as,

\[ v_o = [C_{C_2}] A_1 e^{-E_{A1}/k_B T} + [C_{C_4}] A_2 e^{-E_{A2}/k_B T} = A_o e^{-E_o/k_B T}, \]

where, \( v_o \) is the overall reaction rate of VA-CNTs and can be described as a single Arrhenius function apparently; \( A_o \) is the constant overall
pre-exponential factor; $E_{Ao}$ is the overall apparent activation energy, which is a function of $[C_4]$. Replacing $[C_4]$ by eq. (3.3), we can obtain $E_{Ao}$ as a function of $C_2$. The numerical prediction based on the multiple-reaction-pathway model for the CNT growth rate with respect to $P_{C_2H_2}$ is shown in Fig. 4c. The prediction shows that when enhanced gas-phase reactions of $C_2H_2$ are present, the overall $E_A$ is positively dependent on $P_{C_2H_2}$.

**Figure 3.4** Schematics, numerical prediction, and electrical circuit analogy for the VA-CNT growth kinetics. (a, b) With the help of enhanced gas-phase reactions, secondary products such as $C_4$ and $C_6$ species are produced to approach the catalyst substrate. Gaseous secondary products could participate in the CNT synthesis through reaction pathways, path 3 and path 4, unseen in the CVD without the precursor thermal rearrangement. With no gas-phase reaction, $C_2H_2$ contributes to CNT growth through dissociation followed by bulk diffusion (path 1) or surface diffusion (path 2). (c) Kinetic data predicted by the multiple pathway model. Overall $E_A$ predicted through a simple carbon diffusion mechanism in the absence of gas-phase thermal rearrangement (black) is shown independent of the $P_{C_2H_2}$; and the $E_A$ with enhanced gas-phase reactions depend on $P_{C_2H_2}$. 

![Image of schematics and diagrams related to CNT growth kinetics.](Image)
considerably. (d) A resistor-capacitor circuit analogy for the CNT growth rate based on a multiple pathway mechanism.

The model shows great consistency with our experimental data, as it considers the contributions from additional surface reaction pathways of the secondary gas pyrolysis species derived from the C\textsubscript{2}H\textsubscript{2} feedstock. In other words, the contribution of the pyrolysis product, C\textsubscript{4} species, can render the overall E\textsubscript{A} deviate from a constant value, in the presence of a prominent gas-phase reaction. Consequently, this parallel-pathway model could possibly provide an explanation for our experimental observation of the apparent activation energy with respect to P\textsubscript{C\textsubscript{2}H\textsubscript{2}}.

3.4.4 An Improved Electric Circuit Analogy Incorporating the Activation Energy

To better illustrate the contribution of each reaction pathway to the final CNT product, we propose an analogy between the parallel chemical reactions and an electric circuit, as given in Figure 3.4d. This electric circuit model is composed of resistors (with resistance, R) and capacitors (with capacitance, C) driven by a voltage source. Each resistor-capacitor pair (RC pair) is connected in parallel and share the same voltage across their endpoints. When voltage (E) is applied, the RC pairs draw a charging current to store electrical energy in the capacitor. The larger the capacitance, the more the transient current flows through that RC circuit.

The RC circuit analogy transforms the Arrhenius plot of the CNT growth from the growth-rate–thermal-energy domain to the charging-current–time domain. In the RC circuit analogy, the total charging current (I\textsubscript{total}) is analogous to the overall initial growth rate in the CNT growth kinetics. The total charging current is the sum of charging currents out of each branch (I) of the parallel RC circuit. The current in each branch is a function of R and C values as

\[ I = \frac{E}{R} e^{-t/RC} \]

(3.4)
and thus the total current equals to

\[ I_{total} = E \left( \frac{1}{R_1} e^{-t/R_C_1} + \frac{1}{R_2} e^{-t/R_C_2} + \ldots \right) \] (3.5)

In this analogy, the charging time, \( t \), corresponds to an inverse thermal energy \((k_B T)^{-1}\), the \( RC \) product to \( E_A \); and the voltage over resistance, \( E/R \), to the pre-exponential factor of the CNT growth kinetics model.

Our proposed RC circuit provides a more fine-grained model for the growth kinetics in contrast to the commonly used, simple resistor circuit [210]. While the resistor circuit does provides a corresponding resistor for every reaction step in the CNT production mechanism, the oversimplified approach cannot model the changes in \( E_A \) because the model only employs resistors. Therefore, the classical model fails to deliver a direct physical meaning to \( E_A \). Since \( E_A \) is the focal point of our study, it is crucial to have a direct physical representation of \( E_A \) in the circuit analogy.

Indeed, the RC circuit model can explain the physics of \( E_A \) variance. At time \( t \) of the multiple-RC circuit, the branch of higher \( RC \) value yields large charging current than the branch of lower \( RC \) value does. Analogously, among parallel reaction pathways for the VA-CNT growth, the pathway with lower \( E_A \) would contribute more to the growth rate than the pathway with higher \( E_A \) does, noting that \( RC \sim 1/E_A \). If we use (5) to calculate an apparent \( RC \) value for the entire circuit, the apparent overall \( RC \) value depends on the \( C \) and \( R \) values in each branch. Similarly, the apparent \( E_A \) calculated for the CNT growth having multiple reaction pathways is dependent on the \( E_A \) and the proportionality constants (pre-exponential factor and/or \( \text{P}_{C_2H_2} \) value) of each pathway. Changes of the \( RC \) value in a circuit branch will thus lead to changes in the \( I_{total} \) and the apparent overall \( RC \) value. Likewise, variation in the \( A \) value (caused by a change in \( \text{P}_{C_2H_2} \)) of a certain reaction pathway will affect the apparent \( E_A \) value of the CNT growth. In brief, the RC circuit analogy can provide a powerful model to analyze the \( \text{P}_{C_2H_2} \)-dependent \( E_A \) and the accumulative effect of complex chemical reactions in the CNT growth. Furthermore, the RC circuit analogy offers a flexible platform to model CNT growth kinetics, as it can be extended to cover multiple reaction pathways. This aspect
becomes of particular utility when the gas-phase reactions are even more complex or when multiple species behave as precursor gases.

3.5 Conclusion

The activation energy of the VA-CNT growth deviates from a constant value to higher ones at increased C_2H_2 concentrations when thermal pyrolysis of the feedstock gas is enhanced. In-situ mass spectra and the reacting flow simulation results support our postulate that gas-phase reaction products such as C_4H_4 and C_6H_6 do exist and have a significant influence on the VA-CNT growth. By correlating this deviation of activation energy with a cumulative effect of the secondary pyrolysis products, we proposed a parallel reaction pathway model in conjunction with the Eley-Rideal mechanism. Our parallel reaction model supports the observation of the P_{C_2H_2}-dependent activation energy, which cannot be explained by a simplified model assuming a single rate-limiting step. Our proposed electric circuit analogy illustrates the parallel reaction pathway model by projecting the overall CNT growth rate as the total charging current and the E_A as the inverse RC value in the resistor-capacitator circuit. Our work unveils a complex aspect of the catalytic CVD process and enables rational design of the thermal pyrolysis process for an effective CNT growth at an industrial scale. Further refinement of this model can lead to a deeper understanding and a better control of the CNT CVD. Also, the growth data and the simulation results can collaborate to engender new knowledge on the diameter-selective VA-CNT growth.
4 VA-CNT Structure Control by Optimization of Catalyst-Support Interaction

Parts of this chapter have been published in:


4.1 Abstract

A precise control of the dimension of carbon nanotubes (CNTs) in their vertical array could enable many promising applications in various fields. Here, we demonstrate the growth of vertically aligned, single-walled CNTs (VA-SWCNTs) with diameters in the sub-1.5-nm range (0.98 ± 0.24 nm), by engineering a catalyst support layer of alumina via thermal annealing followed by ion beam treatment. We find out that the ion beam bombardment on the alumina allows the growth of ultra-narrow nanotubes, whereas the thermal annealing promotes the vertical alignment at the expense of enlarged diameters; in an optimal combination, these two effects can cooperate to produce the ultra-narrow VA-SWCNTs. According to micro- and spectroscopic characterizations, ion beam bombardment amorphizes the alumina surface to increase the porosity, defects, and oxygen-laden functional groups on it to inhibit Ostwald ripening of catalytic Fe nanoparticles effectively, while thermal annealing can densify bulk alumina to prevent subsurface diffusion of the catalyst particles. Our findings contribute to the current efforts of precise diameter control of VA-SWCNTs, essential for applications such as membranes and energy storage devices.
4.2 Introduction and Literature Review

Diameter control of vertically aligned carbon nanotubes (VA-CNTs) in the sub-2-nm regime is an exciting challenge. The architecture of vertical arrays of conductive hollow nanotubes has allowed envisioning various applications such as CNT membrane, supercapacitor, passive heat exchanger and sensors [34, 235-237]. Structure-induced performance of these devices lays strong emphasis on the precise control of the geometry of VA-CNTs including the nanotube diameter. Particularly for single-walled carbon nanotubes (SWCNTs) in the applications of electronics and nanofluidics, the diameter is strongly concerned with the band gap and the transport enhancement, respectively.

Despite the great advances in the past years, shrinking the diameters of VA-CNTs below 2 nm in a reliable economic way is still challenging for two primary reasons. First, tiny metal catalyst nanoparticles get thermally unstable and vulnerable to coarsening at temperatures of chemical vapor deposition (CVD). The catalyst nanoparticles are usually formed by dewetting a metal thin film, e.g., Fe, on a metal oxide support layer, e.g., alumina [238-240]. At elevated temperatures, Fe nanoparticles can dewet into islands on the support in order to minimize the surface free energy at the interface they make with the alumina of lower surface energy. The thermal energy at CVD process could also result in coarsening of nanoparticles, especially the smaller ones [241]. The morphological change of the nanoparticles has a direct influence on the diameters of as-grown CNTs by increasing the average value and broadening the distribution. Second, the tinier the catalyst nanoparticles, the more susceptible they are to carbon poisoning (i.e., choking, carbide formation, etc.) and subsurface diffusion. Since individual CNTs are collectively grown in the VA-CNT synthesis, a local drop of the CNT areal density below a critical threshold could lead to crumbling of the vertical alignment and self-termination of the VA-CNT growth [102, 103, 242]. Thus, the carbon poisoning and the subsurface diffusion are the two main mechanisms responsible for the declination of the nanotube areal density and the cease of growth. As a result, the vulnerability of nanoparticles to such factors as coarsening, amorphous carbon encapsulation, and subsurface diffusion, has been curtailing the effective VA-CNT growth in the sub-2-nm regime.
To obtain ultra-narrow VA-CNTs, researchers have investigated a wide ranges of parameters, primarily focusing on three approaches: pre-growth conditioning, CVD parameters, and catalyst engineering[241]. The catalyst conditioning involves the manipulation of the nanoparticle dewetting and reduction conditions such as H$_2$ partial pressure, temperature ramp rate, and exposure time [89, 100, 102]. The CVD parameters comprises growth conditions such as growth temperature, carbon exposure duration, precursor gas composition and dwell time, moisture additives, and so forth [99, 107, 199, 212, 215, 222, 243]. For instance, by balancing the CVD temperature, limiting the C$_2$H$_2$ partial pressure, and rendering catalyst nanoparticles well isolated and sufficiently dense, Youn et al. have reported sub-2-nm-wide CNTs on an iron-on-alumina substrate [104].

Other than the CVD conditions, researchers have long been interested in the catalyst engineering, given the fact that the CNT CVD is a heterogeneous catalysis process. One way of engineering the catalyst is to optimize the preparation method and tailor the composition such as mono- and bimetallic systems [116, 117, 244]. It is not only important to select the right catalyst material but also to prepare the catalyst properly in order to provide the desired nanoparticle morphology and stability. Several research groups have proposed to deposit nanoparticles as catalyst that are small and dense enough to minimize the CNT diameter [118, 245, 246]. Another way of tailoring the nanoparticle size is related to catalyst support engineering. Of the support materials available, alumina and silica are most widely used in the CNT growth. It is observed that CNTs grown on an alumina-supported catalyst have shown the fastest CNT nucleation rate and small diameters with narrow distributions[240, 247], while CNTs formed on a silica-supported catalyst require longer time for nucleation, large diameters, and low areal number densities [238, 239].

A number of recent studies have shed light on the significant role of the alumina support engineering in tailoring the CVD synthesis of VA-CNTs for their growth rate and SWCNT specificity. Noda et al. have proposed that alumina can help facilitate the CNT growth rate by adsorbing carbon precursors on its oxide surface to supply them to catalyst nanoparticles [248]. In addition, it has been suggested that alumina prepared in different techniques can lead to diverse lifetime,
activity, and evolution of catalyst during the CNT growth [249]. Moreover, crystallinity of the alumina has also been reported as an important parameter. Amorphous alumina having high porosity has been preferred and able to result in good yield and fast growth, while single crystalline sapphire has been recognized as an “inactive” support. In light of modifying the alumina property, energetic ions bombarding onto a single-crystalline sapphire layer has been shown to turn the exposed surface into a porous layer, usable as an active catalyst support for the VA-CNT growth [250, 251]. Bearing a potential practicability issue for large scale production, the effect of this method on the resultant nanotube diameters remains to be elucidated. An O$_2$ plasma treatment of alumina has been reported to help inhibit the subsurface diffusion of Fe into alumina, resulting in the large areal density and prolonged activities of the Fe nanoparticles. Modification of the acidity of alumina has also been observed to have an influence on the CNT growth lifetime, efficiency, and the diameter of multi-walled VA-CNTs [123]. Moreover, it has been reported that by adding a very thin layer of alumina over a Fe oxide, an alumina-Fe-alumina sandwich structure could yield small-diameter CNTs with high purity and millimeter-scale lengths [252-254]. The anticipated role of the top surface of alumina is to immobilize nanoparticles during the growth, although a thorough investigation of the underlying mechanism is absent. Despite the notable improvement in understanding the role of alumina in the CNT CVD growth, only a few reports have focused on the relation between the alumina support properties and the VA-CNT diameters, particularly in the SWCNT diameter regime, and therefore it is still challenging to achieve a SWCNT forest in a sub-2-nm diameter range.

Here, we demonstrate the growth of VA-SWCNTs with diameters in a sub-1.5-nm regime by engineering the properties of the catalyst support, i.e., alumina. We first hypothesize that high porosity at the surface and high density (low porosity) in the bulk alumina could inhibit the surface coarsening and the subsurface diffusion of the catalyst nanoparticles. Then, we design a sequential procedure for the alumina treatment that conjoins thermal annealing and ion beaming, with which to grow VA-SWCNTs of ultra-narrow diameters. To understand how this sequential treatment helps safeguard this growth, we analyze the effectiveness of each process and the sequence in a decoupled way. Based on the findings, we explain the mechanism of
engineering the catalyst support for growing a forest of sub-1.5-nm-wide SWCNTs.

4.3 Results and Discussions

Our overarching goal is to understand and optimize the properties of the alumina support to grow the ultra-narrow VA-CNTs. Thermal dewetting of metal thin films into nanoparticles is selected for the catalyst preparation method throughout this investigation. If the dewetted catalyst nanoparticles shall disperse themselves finely, homogeneously and densely on the alumina support, and if they shall keep the dispersion without agglomeration or subsurface diffusion during CVD, the alumina underlayer has to be porous at the surface but needs to remain densified in subsurface zones. Otherwise severe subsurface diffusion could possibly deteriorate the vertical alignment [254], particularly for the growth of narrow nanotubes. Although desired, the task of preventing both the agglomeration and the subsurface diffusion of the catalyst nanoparticles is challenging because of the inverse correlation between the porosity and density of the alumina support.

**Figure 4.1** Sequential treatments of alumina and the as-grown sub-1.5-nm VA-CNT. (a) E-beam deposited alumina is brought to and kept at high
temperature of 800 °C for 30 min and then bombarded by Ar\textsuperscript{+} beam of 600 eV for 1 min before 1-Å-thick (nominal thickness) Fe catalyst is deposited. (b, c) The transmission electron microscope image (scale bar: 2 nm) and the histogram of the as-grown nanotubes show an average mean diameter of 0.98 nm and upper bound of 1.5 nm. The nanotubes are single walled. (d) Raman spectra of the as-grown VA-CNTs for the excitation wavelengths of 785 nm (red), 532 nm (green), and 445 nm (blue). (e) Diameter distribution of VA-CNTs obtained by the present and previous reports.[102, 117, 118, 199, 243-245, 249, 252, 253, 255, 256]

To overcome this challenge, we have conceived a procedure that decouples the control of bulk and surface properties of the alumina support. This procedure utilizes thermal annealing and ion (Ar\textsuperscript{+}) beam treatment to densify the bulk alumina and to change the surface properties, respectively (see Methods for details). A sequential procedure of annealing and ion beam treatment is designed prior to the Fe catalyst deposition (Figure 4.1a). As the result, the Fe catalyst supported by the thus treated alumina layer produced VA-SWCNTs with diameters ranging between 0.5 nm and 1.5 nm (Figure 4.1b,c). Raman spectra (Figure 4.1d) has full width at half maximum of G band is 26 cm\textsuperscript{-1}, and the G-to-D band intensity ratio is 12, which presents the typical features SWCNTs of high quality [84, 257]. The spectra at three excitation laser wavelengths (445 nm, 532 nm, and 785 nm) show prominent radial breathing modes (RBM) between 170 cm\textsuperscript{-1} and 300 cm\textsuperscript{-1}. By knowing the frequency of RBM, the diameters of single wall CNTs are estimated based on the relationship \( V_{RBM} = 234/d + 10\) [258]. Each CNT is associated with a unique pair of indices \((n, m)\) that fingerprints its properties.[259] Raw data of chiral maps is listed in Table 4.1. The chirality map is deduced from RBMs (Figure 4.2), designating the existence of CNTs in the diameter range between 0.8 to 1.5 nm, in excellent agreement with the TEM characterization result of the nanotube diameter distribution. According to the chirality map, one third of the spotted CNTs are metallic, indicating random chiral distribution of the SWCNTs [260]. In contrast, the control sample of as-deposited alumina, to which no treatment had been applied, yielded no vertical alignment despite using the identical catalyst and the CVD condition. This result underpins a critical role of the alumina treatment in the growth of ultra-narrow VA-CNTs. In comparison to the previous reports, the SWCNT diameter distribution we obtained lies among the smallest (Figure 4.1e).
Figure 4.2 Chiral map derived from radial breathing mode (RBM) wavenumber of grown sub-1.5-nm-wide single-walled CNTs grown on sequentially engineered alumina substrate with Fe catalyst of 0.1 nm.

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<td>180.00</td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>1.41</td>
<td>176.02</td>
</tr>
<tr>
<td>12</td>
<td>9</td>
<td>1.43</td>
<td>173.76</td>
</tr>
<tr>
<td>14</td>
<td>7</td>
<td>1.45</td>
<td>171.36</td>
</tr>
</tbody>
</table>

Table 4.1 Table of all assigned (n, m) for CNTs shown in S1. The diameter of CNT, d, is in nm, the frequency of RBM is in cm$^{-1}$.

In order to understand the effect of each treatment on the growth of the VA-SWCNT forest, we compared growth performance (i.e., diameter distribution and length of as-grown nanotubes) on four types of alumina supports: a) as-deposited control; b) annealed only; c) ion-
beam-treated only; and d) annealed and ion-beam-treated sequentially. Except for the support preparation method, the other conditions of Fe catalyst deposition (2 Å by nominal crystal-monitor reading) and CVD (see Methods for details) are identical for various runs unless otherwise specified.

**Figure 4.3** Impact of alumina treatments on CNT diameter and height. CNTs are grown by identical Fe catalyst of 2 Å under same CVD condition on different alumina supports. The diameter distribution of CNTs characterized by TEM images are shown in (a). Ion beam treatment applied on alumina substrate results in a reduction of CNT diameter, as shown by the red arrows in (a); heat treatment applied on alumina leads to slight increase of CNT diameter. The height of CNTs after 5 min of growth on two alumina, ion beam treated (4 μm) and heat plus ion beam treated alumina (77 μm), are characterized by SEM images and are compared (b). The impact of heat treatment condition on diameter of CNTs is illustrated in (c), by comparing the diameter distribution of CNTs grown on heat + ion beam treated (orange) and heat treated alumina (green). Three heat treatment conditions are applied to alumina: 800 ºC 30 min, 800 ºC 120 min, and 950 ºC 30 min.

TEM analysis reveals that the ion beam bombardment on alumina leads to small nanotube diameters, whereas thermal annealing has an opposite effect. When the pristine alumina support was bombarded with Ar⁺ beam (see Methods for details) prior to the Fe deposition, the mean diameter of the resultant CNTs decreased from 3.7 nm to 2.6 nm; similarly, when the annealed alumina support was bombarded with
Ar\textsuperscript{+} beam, the resultant CNT diameter dropped from 4.1 nm to 2.5 nm (Figure 4.3a, red arrows). On the other hand, the thermal treatment resulted in slight enlargement of the CNT diameter. Besides, it turns out that the sequence of the alumina treatment is critical for the nanotube growth rate and the number density; a sequence of annealing prior to the Ar\textsuperscript{+} bombardment led to the growth of VA-CNTs, while the reverse sequence ended up growing short and poorly aligned CNT brushes underlying a random CNT network, likely caused by the growth termination at an early stage (Figure 4.3b). These evidences bolster the effectiveness of our approach for the formation of densely distributed, tiny catalyst nanoparticles towards the ultra-narrow SWCNT forest growth.

However, excessive annealing of alumina for a prolonged duration or at excess temperature deteriorates the effectiveness by causing an undesired increase of the resultant CNT diameters. We compared the diameter of VA-CNTs grown on the Fe catalysts supported by three differently annealed alumina: (A) 800 °C for 30 min, (B) 800 °C for 120 min and (C) 950 °C for 30 min with or without additional ion beam bombardment (Figure 4.3c, orange and green histograms, respectively). Excessive annealing conditions like (B) and (C) broaden and enlarge the CNT diameters, compared with the case (A) undergoing moderate annealing. A moderate thermal annealing is as critical as the ion bombardment for narrowing down the diameters of VA-SWCNTs. For all the annealing conditions, on the other hand, the effectiveness of the ion bombardment towards the CNT diameter shrinkage is reconfirmed (Figure 4.3a).

We reverse the treatment sequence of alumina, i.e. first ion beam treatment and then heat treatment, and compare the diameter and apparent growth rate of VA-CNTs respectively. (Figure 4.4) CNTs grown alumina treated in regular order have average diameter around 1 nm and upper limit around 1.5 nm (Figure 4.4a); while CNTs grown on alumina treated in reversed order have average diameter around 1.78 nm and upper limit around 4 nm (Figure 4.4b). As discussed previously, ion beam treatment creates surface defects and increase porosity, whereas heat treatment heals defects and decrease porosity. For alumina with treatment in reversed order, surface defects and porosity created during ion beam treatment might be demolished by heat treatment, leaving the less defective and porous with high Ostwald
ripening rate, contributing to large diameter and wider distribution in (Figure 4.4b). The apparent growth rate, deduced from the height of CNTs grown after 5 min, is also lower in (Figure 4.4b): its low surface porosity of alumina in may results in large particles with low area number density, contributing to bad alignment of CNTs. In brief, to achieve effective growth of small-diameter VA-CNTs, the sequence of treatments on alumina is critical and should not be altered.

**Figure 4.4** Role of the treatment sequence on the structure of CNTs. Representative TEM and SEM images of CNTs grown on alumina support with first heat and then ion beam treatment (a) and on alumina treated in reversed order (b) that is first ion beam then heat. Compare CNTs grown on alumina (a) and (b), the prior one has small average diameter with narrower distribution, better vertical alignment as well as high apparent growth efficiency.

To elucidate the formation and evolution of the catalytic nanoparticles on the alumina treated above, we characterized the surface morphologies (size and number density) of Fe nanoparticles formed atop four different types of the alumina supports using atomic force microscopy (AFM). AFM scanning measures the Fe particle heights of the Fe-on-alumina samples that had been annealed altogether in an H₂/Ar atmosphere (see Methods for details) without exposure to C₂H₂.
The resultant nanoparticle morphology represents the nanotube nucleation centers that have evolved on the surface from the initial thin film \[209, 225, 261\]. We observe that the Fe films deposited on the ion-beam-bombarded alumina converts to nanoparticles that are higher in density and smaller in diameter than those on the as-deposited or solely annealed alumina supports (Figure 4.5a, indicated by red arrows). Alumina annealing alone, on the other hand, turns out to decrease the nanoparticle density (Figure 4.5a, black arrow) and broaden the nanoparticle sizes (Figure 4.5c, blue arrow). The AFM observations and the TEM analysis (Figure 4.3) collectively support our claim that the alumina surface can influence the evolution of the catalyst particles responsible for the dimension of nanotubes nucleated from them. The AFM-resolved nanoparticle heights are slightly smaller than the corresponding CNT diameters in general, possibly attributable to imperfect hemispherical or elliptical geometry of the dewetted particle \[262, 263\].

**Figure 4.5** AFM characterization of catalyst nanoparticle density and size on various alumina support. The sample with Fe NANOPARTICLEs was directly cooled down in Ar after dewetting in H\(_2\)/Ar mixture without carbon exposure. (a) Density of as formed nanoparticles. The particle density is lower on heat treated alumina (black arrow) and higher on ion beam treated and heat + ion beam treated alumina (red arrows). (b) Topology images of catalyst substrates measured by AFM. The scale bar is 100 nm. (c) Size distribution of nanoparticles. The particle size decreases on alumina with ion beam treatment (red arrows) and increases on alumina with heat treatment (blue arrow).
To understand the way how the thermal and ion beam treatments alter the properties of the alumina support, we carried out X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry. Since X-rays have a penetration depth of only a few nanometers, XPS analysis is a suitable tool for probing the hydroxyl (-OH) content and the O-to-Al atomic ratio (O/Al ratio) on the surface and subsurface of the alumina. The O 1s core level peak of stoichiometric alumina is located at 531.4 eV (Figure 4.6a, blue peaks). In addition to that, we observe shoulders by an additional peak at 532.5±0.5 eV, an indicator for the existence of -OH bonds. Remarkably, this asymmetry introduced by -OH is the most conspicuous on the ion-beam-modified alumina and is hardly noticeable on the solely annealed one. In order to quantify the elemental composition in the topmost layer of the alumina support, we scaled the background subtracted, raw peak areas of the analyzed core levels to relative sensitivity factors (i.e., 0.66 for O 1s and 0.185 for Al 2p) [264] and determined the ratio of incorporated oxygen to aluminum (O/Al ratio). All films are slightly oxygen-rich in comparison to stoichiometric alumina (Al₂O₃, O/Al ratio=1.5). Particularly, the ion bombardment is found to enrich the surface oxygen content of alumina significantly (Figure 4.6b, red arrows). As ion beam-treated alumina exhibits enhanced surface porosity, it also provides more adsorption sites for H₂O, which is most likely the origin of the observed OH species. Annealing proves this hypothesis by bringing back the O/Al ratio towards the stoichiometric ratio. Finally, the sequentially engineered alumina (annealing followed by ion bombardment) exhibits a moderate change of the O/Al ratio, lying in between the annealed and ion bombarded alumina.

Scanning ellipsometry allows to characterize the optical properties of dielectric thin films; it can provide information about the changes in the bulk density (or porosity) of alumina because the refractive index is correlated positively ( inversely) with the bulk density (porosity) of the thin film (Figure 4.6c). Crystalline sapphire (black line) as a reference shows the highest density and refractive index. The refractive index of alumina decreases in the following order: sapphire (black) > annealed (blue) > annealed and ion beamed (light blue) > as-deposited (red) > ion beamed (green). This trend indicates that thermal annealing and ion bombardment can increase and decrease the apparent density of alumina, respectively. We speculate that the former treatment affects the bulk alumina density, whereas the latter
induces defects near the surface [265]. Sequentially (annealing followed by ion bombardment) treated alumina is denser than as-deposited or ion beamed alumina yet less dense than annealed alumina. The relatively low bulk density of the sequentially treated alumina is attributed to the contribution of a porous surface layer. Excessive annealing further densifies alumina; the refractive index (bulk density) of alumina treated by various heat conditions decreases as follows: 950 ºC 30 min > 800 ºC 120 min > 800 ºC 30 min > as-deposited.

**Figure 4.6** Comparison of four types of the alumina support for surface chemical composition and bulk density via X-ray photoelectron spectra (XPS) and spectrometric ellipsometer. (a) To calculate the O/Al ratio, each O 1s spectra in XPS measurements is decomposed into contributions from Al-OH (magenta) and Al-O (blue). Such decomposition is shown for the O 1s spectra obtained at surface of as deposited, ion beam treated, heat treated, and heat + ion beam treated AlOx. (b) The ratios of O to Al elemental composition (black, no pattern) and the ratios of Al-OH to Al-O (blue, slanted line pattern) in the alumina films based on the
quantitative analysis of the O 1s and Al 2p core level spectra. (c) Index of refraction as a function of wavelength for various alumina supports. The curves were simulated to fit the Cauchy model. The crystalline sapphire (black) has the highest refractive index, indicating the lowest porosity. The as-deposited alumina (red) increases its refractive index upon thermal annealing but decreases after ion bombardment (green). The refractive index of sequentially treated alumina (light blue) lies in between those of the annealed and as-deposited alumina.

To sum up, the ion beam treatment of alumina provides a structure with near-surface porosity leading to enriched -OH group and low apparent density (high porosity), while thermal annealing densifies alumina, with possibly removing physisorbed water (-OH) and reorganizing the atoms. The moderately enhanced value of the O/Al ratio in the sequentially engineered alumina is explainable by the cumulative effect of annealing and ion beaming. Upon annealing, for example, alumina is likely to be hardened and densified [266].

To obtain elemental information of the engineered alumina, we performed high angle annular dark-field scanning TEM (HAADF-STEM) and EDS mapping during TEM measurements by FEI Talos F200X. We compared alumina with ion beam treatment (Figure 4.7a) and with heat + ion beam treatment (Figure 4.7b), and found very similar elemental distribution. Al and O are found spanning over 30 nm, corresponding to the alumina thin film. Below alumina dominant Si signal is observed, signalize the Si wafer. On top of alumina, a 5 nm layer of Au is detected. Au layer was deposited intentionally as a conductive layer to avoid charging effect of alumina during lamellar preparation by focused ion beam (FIB). On very top of the sample, we observe granular structure (from HAADF images) in both samples, which could be associated to the 100 nm of Pt layer coated in order to protect alumina from overheating and beam damage.
Figure 4.7 High resolution transmission electron microscope (HR-TEM) cross-section images of alumina and their fast Fourier transformations (FFT). The cross-section images marked with three selected areas representing top, middle and bottom part (height × width = 2 nm ×33 nm) and their fast-Fourier transformation (FFT) images of the two types of alumina: (a) the ion beam treated (type A) and (b) first heat and then ion beam treated (type B). Both alumina thin films are around 33 nm and deposited on Si (100) wafer. The pixel intensity profile with respect to radius (q, spacing in reciprocal space) is plotted by adding up all the pixel intensity at the same radius (axis value q in reciprocal space) from the corresponding FFT images.

For an in-depth analysis of the potential phase change caused by the thermal annealing and of the penetration depth of the ion beam bombardment, we carried out high-resolution TEM and fast Fourier transformation (FFT) across the film thickness of the ion beamed alumina with and without the annealing pretreatment at 800 °C for 30 min (Figure 4.8). According to the cross-sectional TEM images, both alumina samples are polycrystalline having crystalline domains of a few nanometers. For a detailed analysis, we selected three strips, each as thick as ~2 nm, across the alumina thickness to investigate via FFT their variation in the crystallinity with the film depth. For the ion beamed alumina without preannealing (Figure 4.8a), FFT of the top strip (A-i) shows a ring pattern with no distinctiveness implying close to an amorphous phase; while the inner strips (A-ii, A-iii) exhibit recognizable spots in the pattern that hint a certain degree of a crystalline phase. The corresponding intensity profiles summed up along a q axis also show difference between the surface layer (A-i) and the bulk layer (A-ii, A-iii) in that more distinctive patterns are seen in
the bulk. This observation indicates that the energetic ion bombardment used in this investigation indeed amorphizes the surface of the alumina support down to a few nanometers with leaving the subsurface layer intact.

**Figure 4.8** Cross section analysis of the alumina layers via high-resolution transmission electron microscopy (HR-TEM) and fast Fourier transformations (FFT). The cross-section images marked with three selected areas representing the top, middle and bottom parts (height × width = 2 nm × 33 nm) and their fast Fourier transformation (FFT) images of (a) the ion-beam-treated alumina (type A) and (b) the annealed-and-ion-beam-treated alumina (type B). Both alumina thin films are ~33 nm and deposited on a Si (100) wafer. The pixel intensity profile with respect to radius (q, spacing in reciprocal space) is plotted by adding up all the pixel intensity at the same radius from the corresponding FFT images.
For the ion beamed alumina with preannealing (Figure 4.8b), FFT shows a diffraction pattern for all strips indicating a polycrystalline structure all over the alumina film, with no distinctive amorphous phase near the ion bombarded surface. The annealing-induced crystallization [266] is indeed confirmed by the peaks in the intensity profile (e.g., B-ii and B-iii as opposed to A-ii and A-iii). In the intensity profile, a pattern at low q number observable for bulk strips (B-ii, B-iii) is different from the one for the surface strip (B-i). This observation suggests that the annealed alumina has a crystalline phase throughout the entire thickness, although the crystalline phase very near the surface may differ from that of the bulk to some extent.

Figure 4.9 Schematics of the nucleation and evolution of catalyst particles on various alumina supports.

We schematically describe the Fe catalyst evolution and the related VA-CNT growth for the four variations of the alumina support, as follows. Prior to the CNT nucleation, the e-beam deposited Fe thin film dewets and transforms into catalytic nanoparticles at the catalyst-alumina interface upon exposure to the hot reducing atmosphere (see Methods for details). The density and the size of the resultant catalyst particles
depend strongly on the surface energy (e.g., defects, porosity, etc.) of alumina. The ion bombarded alumina ends up bearing an amorphized surface layer, lowering the surface energy, and thus forming densely packed nanoparticles (Figure 4.9b,d). In contrast, the annealed alumina becomes increasingly crystalline and densified, leading to high surface energy and thus prone to formation of enlarged nanoparticles at a relatively low number density (Figure 4.9c).

After the dewetting stage, C_2H_2 is introduced into the chamber at CVD temperature of 800 °C for the CNT growth. The initial number density of CNTs is likely correlated with the initial number density of Fe nanoparticles, though the Fe nanoparticles located at the base of the growing CNTs can continue to evolve through Ostwald ripening and subsurface diffusion. The particle coarsening at the surface is the most severe for the annealed alumina and the least expressed for the ion bombarded alumina, possibly attributable to the high and low surface energies, respectively. The subsurface diffusion of the Fe atoms or clusters is predominant for the (solely) ion bombarded alumina, and can result in the deficiency of catalysts on the alumina surface, potentially deteriorating the CNT vertical alignment.

Finally, the ion bombarded alumina creating the low-energy surface layer enriched with -OH groups, atop which the Ostwald ripening can be desirably suppressed, can allow for the growth of ultra-narrow VA-SWCNTs (Figure 4.9b); and if the ion bombardment is combined with proper preannealing of alumina, synergy could be achieved that enhances the areal number density and the catalytic activity of the catalyst nanoparticles but inhibits the otherwise vigorous subsurface diffusion, hence likely leading to sub-1.5-nm VA-SWCNTs (Figure 4.9d).

### 4.4 Experimental Methods

#### 4.4.1 Preparation of the alumina support layer

We deposited a 30-nm-thick alumina film on a Si (100) wafer by electron beam evaporation (Univex 500, Leybold) at a deposition rate of 0.2 Å s^{-1} at the chamber pressure in the range of 1-2×10^{-6} mbar. Two types of the postdeposition treatments were applied to the as-deposited alumina – thermal annealing and ion beaming – alone or in
a combined way. The control group is the as-deposited alumina. The standard annealing temperature and duration are 800 °C and 30 min and have been varied for control experiments to be 800 °C and 120 min 950 °C for 30 min, respectively. By bombarding the as-deposited alumina with Ar\(^+\) beam (Oxford Ionfab 300Plus) at 100 mA, 600 eV at an impingement angle of 20 ° for 1 min, we obtained the ion-beam-treated alumina. A sequentially treated alumina was obtained by annealing the as-deposited sample followed by the Ar\(^+\) beam bombardment. The sequence was reversed in order to test its effectiveness.

### 4.4.2 Fe catalyst preparation and the catalytic CVD.

On the prepared alumina support, a thin layer of Fe is deposited via electron beam evaporation (2 Å by nominal crystal-monitor reading). During the deposition at 0.03 Å s\(^{-1}\), the chamber pressure was kept at 1-2×10\(^{-6}\) mbar. CVD of VA-CNT was carried out in a cold-wall vertical reactor (Black Magic Pro\(^{\text{TM}}\), Aixtron AG) with a gas shower head. The dual heaters at the gas inlet and the sample stage and the cold-wall design allow fast heating and cooling.

Prior to growth, the chamber was cleaned by high flux H\(_2\) of 1000 sccm at 800 °C for 10 min. After the chamber was cooled down to 100 °C and below, catalyst substrates were loaded onto the sample stage. The sample stage was heated up at 200 °C per min by dual heaters to an annealing temperature and kept at the temperature for 40-60 sec. During the annealing, 200-sccm Ar and 800-sccm H\(_2\) were flown as a carrier gas and a reductant. The total gas pressure was kept at 8 mbar. Following the annealing, the chamber was quickly cooled down to and stabilized at 700 °C within 40 sec, before 5 sccm of C\(_2\)H\(_2\) was added into the gas flow for the CNT growth. After the growth, the CVD reactor was cooled down in Ar, and the samples were taken out into the ambient below 400 °C.

### 4.4.3 Characterizations.

Pristine CNT forests were analyzed by scanning electron microscopy (Hitachi), high resolution transmission electron microscopy (Philips CM 12) at 100 keV, and Raman spectroscopy with three wavelengths of
785 nm (Renishaw RM 1000), 532 nm and 445 nm (WiTec CRM200). The atomic force microscope images were taken with an Asylum Research, MFP-3DTM in the tapping mode at a scan rate of 1 Hz and a cantilever oscillation frequency of ~279 kHz for a scan size of 1×1 μm². A super sharp tip with a tip radius less than 5 nm (Nanosensors™, SSS-NCHR) was used for an enhanced resolution. The images acquired were flattened to remove tilt in the image. In all measurements, nanoparticle size as opposed to width were measured because heights are unaffected by the tip radius. Characterization of the film chemical composition and stoichiometry was performed on alumina (AlOₓ) thin films on SiO₂ by X-ray photoelectron spectroscopy (XPS) (PHI Quantum) in normal emission using monochromatic AlKα radiation (hv=1486.7 eV) and a hemispherical electron analyzer. The refractive index of the alumina samples investigated by XPS was measured by a spectroscopic ellipsometer (SENTECH SE850). The measurements were carried out in a wavelength range between 400 nm to 900 nm. The angle of incidence was fixed at 70°. The change of refractive index indicates changes in the density of the films. A generic model was used with the following layer scheme: air/alumina/native oxide (silica)/silicon.

\[
n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (4.1)
\]

\[
\kappa(\lambda) = 0 \quad (4.2)
\]

The refractive index of the overall alumina film was fitted using an equation of a Cauchy transparent layer[267], which could be fitted to dispersion formulas to calculate the real (n in eq. (4.1)) and imaginary (κ in eq. (4.2)) parts of the complex refractive index. In eq. (4.1), A (dimensionless), B (nm²), and C (nm⁴) are material-specific constants influencing the curve fitting at long, medium, and short wavelengths (λ), respectively.

### 4.5 Conclusion

We investigated the optimal requirement for the alumina support towards the CVD growth of ultra-narrow VA-CNTs. By applying thermal annealing followed by ion beam treatment on the e-beam deposited alumina, we demonstrated the growth of sub-1.5-nm-wide
VA-SWCNTs with a mean diameter of ~1 nm, which has not been obtained otherwise on the as-deposited alumina. Microscopic and spectroscopic characterizations reveal that the ion beaming on the alumina is effective in decreasing the catalyst particle sizes required for small SWCNT diameters, since it can amorphize and enrich the alumina surface with OH groups to facilitate the formation of tiny nanoparticles. Through densifying the alumina, on the other hand, the annealing can enlarge the size of the catalyst particles yet inhibit the subsurface diffusion of Fe to sustain the CNT vertical alignment. These findings allow to conceive an alumina treatment condition optimal for the ultra-narrow VA-SWCNT growth, i.e., proper thermal preannealing followed by ion beam bombardment, eventually leading to one of the narrowest SWCNTs in a vertically aligned fashion to date on a Fe catalyst system, a breakthrough that can provide a guideline for the tailoring of CNT diameters. Our understanding of the underlying mechanism, if generalized, is potentially extendable to other transition metal catalyst systems for efficient VA-CNT growths for electronics and nanofluidics.
5 Graphene Growth Kinetics and Layer Control

Parts of this chapter have been submitted for publication in:


Parts of this chapter have been published in:


5.1 Abstract

Cu has proven to be the most widely adopted catalyst material for producing polycrystalline graphene layers. State-of-the-art Cu-based CVD for the graphene synthesis has been evolved to approach a point where it can yield almost as good electronic quality as an individual graphene flake exfoliated mechanically while scaling up the growth to meters. Although monolayer graphene has a zero band gap limiting its potential applications, AB-stacked bilayer graphene reportedly has a tunable band gap under electric fields and thus attracts a great attention. In this chapter, we first review the growth mechanism and structural control of the monolayer graphene on Cu by CVD. In the second part, we report the kinetics and termination mechanism of the bilayer graphene growth on Cu, by decoupling the growth of the two layers via a growth-and-regrowth scheme. We observe, for the first time, that the secondary layer growth follows Gompertzian kinetics. Our observations affirm the postulate of a time-variant transition from a mass-transport-limited to a reaction-limited regimes and identify the mechanistic disparity between the monolayer growth and the secondary-layer expansion underneath the monolayer cover. It is the continuous carbon supply that drives the expansion of the graphene secondary layer, rather than the initially captured carbon amount, suggesting an essential role of the surface diffusion of reactant.
adsorbates in the interspace between the top graphene layer and the underneath copper surface. We anticipate that the layer selectivity of the growth relies on the entrance energetics of the adsorbed reactants to the graphene-copper interspace across the primary-layer edge, which could be engineered by tailoring the edge termination state. The temperature-reliant saturation area of the secondary-layer expansion is understood as a result of competitive attachment of carbon and hydrogen adatoms to the secondary-layer graphene edge.

5.2 Monolayer Graphene

5.2.1 Growth Kinetics

CVD of graphene on Cu has stimulated intense interest since its debut. The growth of graphene on Cu is a surface reaction and has self-terminating nature due to the low carbon solubility of carbon in Cu. However, graphene has not yet made a major leap into industry, especially for electronic applications, due to the fabrication challenges. That is, the growth terminates when monolayer covering is complete. Notably, the CVD method involves numerous tunable parameters such as the choice of catalyst, temperature, carbon precursor etc. On one hand, the large number of tunable parameters increases the complexity of the experimental design; on the other hand it enables a great potential to tailor the properties of graphene by controlling the growth conditions. For controlling the properties of graphene grown, it is critical to understand the primary growth mechanism at play during CVD, which remains the major hurdle to overcome.

Here, we focus on the time dependence of the growth to understand the fundamental mechanisms that govern the CVD of graphene. The information about the growth rate can be extracted by observing the variation in graphene flake size over the growth time. Although real-time observation of a Ru-based graphene growth using low energy electron microscopy (LEEM) has been reported, it is challenging to employ this technique for Cu due to low carbon density and substrate sublimation [80, 268]. As such the literature on the Cu-based CVD kinetics is, at present, rather limited. Recently, CH₄-based graphene CVD investigations by Chhowalla and colleagues have proposed a supersaturation-driven growth, a claim that attributes the entire
growth to depletion of the initial population of the carbon adatoms from the surface [158]. An exponential-like kinetics curve was fitted by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) crystallization model [269], with the assumptions of instant nucleation and carbon-attachment-limited growth, where they incorrectly neglected any contribution of the additional hydrocarbon input during the growth. Their fitting implied that the growth saturates and a continuous graphene layer can never be achieved unless there is sufficient carbon source available at the initial growth stage. Based on similar assumptions, the continuity of the graphene layer can be modeled as a function of the ratio of the \( CH_4 \) partial pressure to the square of the hydrogen partial pressure: \( P(CH_4)/P(H_2)^2 \).

Growth continuity is achieved for partial pressure ratios of > 0.01 for growth temperatures greater than 900 °C [270]. Other carbon precursors such as \( C_2H_4 \) can undergo a more complex reaction cascade, due to the wide number of thermally dissociated intermediaries, as well as a range of possible dehydrogenation processes on the Cu surface. Using a \( C_2H_4 \)-based CVD system, Park and colleagues have proposed a Gompertzian sigmoidal kinetics for graphene growth, indicating that the growth is not only influenced by supersaturation but also by continual hydrocarbon supply as well as associated surface adsorption/desorption dynamics [153].

### 5.2.2 Reaction Energetics

Determination of the reaction energetics is critical in order to determine the rate-limiting processes during the CVD growth. The associated energy barrier for each of the possible reactions compares the energetic weight of the corresponding step in the overall reaction potential scheme. When the hydrocarbon feedstock comes in the hot CVD reactor, gas-phase reactions could thermally rearrange it prior to adsorption [192]. However, unlike the rich literature on the gas-phase reactions involved in carbon nanotube growths with often employing in-situ mass spectroscopy [199, 271, 272], analogous study for probing the growth atmosphere during the graphene growth is not abundant. Moreover, since the adsorption energy barrier of most hydrocarbons on Cu is negligibly small (approximately 0.1 eV) [273], any transiently derived \( C_xH_y \) species formed in the gas phase may rapidly adsorb, disabling direct measurement and leading to the complexity of the
underlying catalytic reactions. Moreover, thermal variations within CVD reactors only support the formation of such transients in hot zones particularly, which further complicates direct measurement. Currently very little is known about these hydrocarbon reaction cascades on Cu. Consequently, it is very difficult to make any assertions on the effects of the gas-phase reactions on the overall CVD process.

Carbon reactant diffusion follows hydrocarbon adsorption [274, 275]. The energy barrier for the diffusion is also low, typically less than 1 eV on Cu [273, 275]. Thus, under equilibrium conditions diffusion is rather unlikely to be a rate-limiting step. Diffusion may become dominant under certain conditions, however, in particular when the hydrocarbon reactions are simpler and diffusion occurs at the subsurface level. Nie et al. have concluded that diffusion is the plausible rate-limiting mechanism when pure carbon is used as the precursor on Cu (111) surfaces under ultrahigh vacuum conditions [268]. Besides surface diffusion, gas diffusion can particularly be important under atmospheric-pressure chemical vapor deposition (APCVD) [276]. During APCVD a boundary layer forms above the substrate surface, and gas diffusion through this boundary layer could become rate limiting. Care must be taken when extracting the activation energies from the resultant Arrhenius curves. In order to determine correct energy barriers responsible for chemical processes, these kinds of mass-transport-limited regime must be ruled out.
When gaseous transport of hydrocarbon is not the limiting factor, catalytic reactions on the Cu surface determine the rate of graphene crystal enlargement. Two main reaction types occur on the surface: (1) a dehydrogenation cascade, which may also involve dissociation of the radicals depending on the carbon precursor, and (2) attachment of carbon in the form of adatom, chain/cluster or hydrocarbon at the crystal edges of growing graphene. The exact nature of these reactions is elusive. A simplistic diagram that displays the approximate energy levels of the adsorption and dehydrogenation is shown in Figure 5.1 [154]. The dehydrogenation energy barrier indicates that the overall reaction is unfavorable and must be supported by excessive hydrocarbon feed. This finding also suggests that reactive precursors can be used for graphene growth at lower temperatures because once these species are adsorbed, desorption would become more difficult.

Which reaction step of the entire graphene growth process should be regarded as rate-limiting is currently in dispute. Accurate measurement of $E_A$ is required for the determination of the reaction that determines the growth speed. For a CH$_4$ precursor Kim $et$ $al.$ have found out an $E_A$ of 2.6 eV [158] and concluded that the carbon adatom attachment (ca. 2 eV energy barrier) [82] is the rate-limiting step, with claiming that the dehydrogenation energy barrier is lower (1.7-1.9 eV) [277]. The species that attach to the flake edges are also widely debated. While some reports focus on the adatoms [158, 270, 278], there are also reports that compare different species to conclude that few-carbon-atom chains are also important reactant species [279]. An increase in the CVD pressure has also been claimed to favor carbon chains versus adatom formation [280]. Alternatively, Celebi $et$ $al.$ have pointed out that the attachment is not the limiting step; instead, a reaction cascade of the dissociative dehydrogenation on Cu determines the growth rate [153]. The reported $E_A$, peaking at 3.1 eV, was found to be time-dependent, as a result of the dispersive nature of this reaction cascade [281-283]. However, the precursor used in this study (C$_2$H$_4$) may well support a more complex reaction scheme than the simpler hydrocarbon (CH$_4$) [284]. For even more complex precursors the
understanding of the associated reactions is much weaker. More investigations are necessary to elucidate the reactants and mechanisms of the reactions.

5.2.3 Crystal Nucleation

Most carbon precursors, such as CH$_4$, C$_2$H$_4$, C$_2$H$_2$ and similarly reactive hydrocarbons, readily chemisorb onto faceted Cu surface and face only a comparatively small energy barrier on the order of 0.1 eV [273]. As the adsorbed carbon species, the form of which is still unknown at present, populate the surface and subsurface, supersaturation is reached. The surface defects, facets and lattice impurities then trigger heterogeneous nucleation. Direct experimental evidence of the growth nucleation at lattice defects, a scratch in this instance, was observed [148]. Upon initial nucleation these graphene seeds begin to deplete the nearby solid solution of carbon reactants. The form of these reactants is disputed, with indications ranging from carbon adatoms [158] to carbon clusters [279] or even hydrocarbons [273, 285]. As the nucleation is governed by the initial carbon supersaturation of the catalyst and the availability of suitable lattice defects, the hydrocarbon partial pressure and the catalyst temperature determine, in part, the spatial number density of the nucleation events. Figure 5.2a shows a reduction in the nucleation density caused by depletion of the available CH$_4$ gas (Figure 5.2b), which reduces the number of available carbon reactants at the moment of the seeding event [274]. Any disturbances in the gas flow related to local facets or turbulence, may also cause spatial inhomogeneity in the nucleation distribution, which is often critically important in horizontal-flow tube furnaces with short precursor residence time that constitute perhaps the most common type of CVD systems. The nucleation density is proportional to decreasing temperature and increasing hydrocarbon partial pressure as well as flow rate (largely for atmospheric pressure CVD) [72]. Temperature also determines the degree of supersaturation because the carbon capture and reactant desorption rates depend highly on temperature [286]. Figure 5.2c shows that at temperatures the nucleation is limited by the capture events of the reactants with an activation energy ($E_A$) of ca. 1 eV, while at higher temperatures desorption becomes the dominant physicochemical mechanism with a higher $E_A$ of ca. 3 eV [158].
Figure 5.2 Nucleation density. (a) (1-4) Optical photograph and micrographs of the Cu foil after 1 min graphene growth at 1000 °C in a horizontal tube furnace. (b) Schematic of the carbon source distribution near the catalyst surface for the horizontal flow, adapted from ref. [274] (c) Arrhenius plot of the nucleation density on a Cu foil. Higher slope curve indicates the desorption-limited nucleation regime with an $E_A$ of 3 eV. Higher slope indicates the desorption-limited nucleation regime with an $E_A$ of 3 eV, while the lower-slope represents capture-controlled regime with an $E_A$ of 1 eV, adapted from ref. [153].

5.2.4 Crystal Morphology

Graphene grown by CVD is polycrystalline. The flake crystallinity and edge morphology dramatically influence the physical and chemical properties of the as-synthesized graphene, in particular charge mobility. This sub-section addresses competing mechanistic models that determine the crystal morphology. The morphologies reported so far can be largely described as a mixture of dendritic or hexagonal geometries, as well as compound structures. Substrate and growth conditions are certainly responsible for the way how the crystal enlargement occurs.

Wofford et al. have reported in-situ observations of four-lobed flake enlargement on Cu (100) under ultrahigh vacuum using a pure carbon precursor [287]. The growth was claimed to be attachment-limited.
The rate of flake enlargement is orientation dependent and has two-fold symmetry as a result of the interaction between the six-fold and four-fold symmetries of the graphene and Cu, respectively. However, a similar study by Nie et al. states that for Cu (111) surfaces the flake morphology changes from dendritic to hexagonal by simply increasing the temperature [268]. They rationalized these findings via a diffusion-limited model. Indeed, unlike surface diffusion on Cu (100), carbon adatoms diffuse through sub-surface sites on Cu (111), which requires surfacing of the adatom, and thus manifests higher energies compared to attachment-limited systems. However, this surfacing mechanism is yet to be explained in any great detail. At higher temperatures on Cu (111) the graphene crystal also presents lobed geometries that are coupled to the six-fold symmetry of the substrate due to the inhomogeneous density distribution of Cu steps. Regarding the crystallinity, the hexagonal crystal at higher temperatures has more uniform crystalline orientation compared to the dendritic crystal. However, when such crystals enlarge and grow over catalyst step edges, the crystalline orientation may change by up to 3°.

During the thermal dissociation of the hydrocarbon precursor atomic hydrogen is liberated. Thus, the effect of concomitant lattice etching may not be neglected during growth. Vlassiouk et al. have reported etching of the graphene crystal by excessive hydrogen during the growth [288]. The reported etch rate was low for zigzag edges, thereby favoring the hexagonality of the crystal. The flake size initially benefits from the catalytic role of hydrogen, until etching becomes dominant at higher \( \text{H}_2 \) partial pressure. However, the role of hydrogen on etching is disputed. A contrasting study by Choubak et al. claimed that it is the \( \text{O}_2 \) impurities in the \( \text{H}_2 \) line that might cause the observed etching of graphene crystals [289]. Indeed, negligible etching of graphene occurred when Celebi et al. grew equally graphitic graphene crystals with and without a \( \text{H}_2 \) ballast and under typical \( \text{H}_2 \) partial pressures during growth. Nonetheless, regardless of the exact etching species, perhaps the most important finding about the graphene flake morphology is that the degree of hexagonality is correlated with total pressure of a reacting chamber [288, 290]. APCVD growths report hexagonal flake shapes with good crystallinity [288], although the reason for this behavior is unclear. Associated explanations include various mechanisms that occur at higher pressures, namely: (1) gas diffusion limitation [276]; (2) prevention of the Cu step advancement.
due to the suppression of Cu sublimation [153, 268]; and (3) difference in the carbon-to-crystal-edge attachment mechanism related to formation of carbon chains on the Cu surface [279]. Hexagonal morphology is more favored compared with the dendritic morphology for better grain crystallinity and connectivity.

5.2.5 Layer Uniformity

However, even for high quality monolayers, two or more additional layers often exist with covering the catalyst surface area up to a few percent of it. These layers result from secondary nucleations that occur at areas that are covered by already growing crystals. Conflicting reports exist on the nature of these nucleations. Robertson et al. have used an atomic force microscopy data to claim that the secondary layers exist on top of the primary layer [291]; however, equivalent surface profiles can also occur when these secondary nucleations are under the primary layer. Furthermore, it is counterintuitive that secondary growth can be catalyzed on top of the primary graphene layer. Other reports indicate the additional layers grow under the first, where the growth is still catalyzed by the Cu and supported by diffusion of the carbon reactants [151]. This claim has been recently supported by Kong and colleagues through carbon feedstock alteration between C$_{12}$ and C$_{13}$ [292].

Various strategies can be employed to minimize the formation of the secondary layers. Han et al. have presented a pulsed supply scheme of the CH$_4$ precursor with incubation intervals designed to allow the excess reactants to be consumed by the first layer [293]. When the excess reactants exist, the probability of having additional nucleations under the first layer is higher. Indeed, Wassei et al. have revealed that increasing the carbon content in the precursor gas can promote secondary nucleations [293]. Alternatively, a carbon sink under a thin catalyst layer can also be used to limit excessive carbon content on the surface. However, this method has only been demonstrated for graphene growth on Ni thin films, with a Mo underlayer acting as the carbon sink [294].
5.3 Bilayer Graphene

5.3.1 Introduction

Bilayer graphene has received a significant attention because of its rich electronic properties.[295] Particularly, high-quality AB-stacked bilayer graphene exhibits a tunable bandgap up to 250 meV when a transverse electric field is applied,[296-298] distinguishing itself from semimetallic monolayer graphene of zero-bandgap dispersion.[299] Numerous efforts have been made to open up the band gap in the monolayer graphene yet often at the cost of drastic degradation of carrier mobility.[300] As a result, the AB-stacked bilayer graphene serves as a promising alternative in such potential applications as field-effect transistors (FETs) [301], pseudospintronics [302], and so forth. Among various graphene synthesis methods, chemical vapor deposition (CVD) has been widely accepted as a promising and effective approach and thus been developed in order to provide graphene sheets with various crystallinity and layer structures in a scalable, inexpensive and transferable manner [303].

To date, a variety of catalysts have been applied to synthesize electronic-quality bilayer graphene. According to the properties of the metal catalyst, CVD growth of graphene can be categorized to follow two growth mechanisms, one via precipitation and another via surface-mediated reaction. Generally, the precipitation-driven growth appears in metal having high carbon solubility and low stability of carbide formation, such as Ni [71, 304, 305]; whereas the surface-mediated growth prefers metals with low carbon affinity and/or solubility, such as Cu [84, 85]. Graphene grown on pure Ni by precipitation requires careful control of carbon dissolution and precipitation because otherwise it easily forms inhomogeneous areas of randomly stacked graphene multilayers. Recent reports of graphene grown on a Cu-Ni alloy have shown mostly AB-stacked layer structure [306], although the Ni involvement could potentially complicate the delicate precipitation process. The reason for the AB-stacking in this Cu-Ni alloy, however, is not fully elucidated. In contrast, graphene grown on Cu by surface-mediated reactions does not involve bulk diffusion or precipitation resulting in better quality and layering uniformity [84]. The CVD of monolayer graphene on Cu is by and large robust and
repeatable, owing to the self-limiting nature of the surface-mediated growth.[151] The large-scale production of monolayer graphene on Cu with a speed up to 500 mm/min has been realized by a roll-to-roll method [166, 307]. Meanwhile, the growth kinetics of monolayer graphene on Cu has been investigated systematically [153, 158, 204, 276]. It is reported that the growth of monolayer graphene based on C$_2$-species precursors follows a Gompertzian sigmoidal kinetics, underscoring the contribution of a continuous carbon supply rather than crystallization from a supersaturated solution [153].

Given the prominent success of Cu in the monolayer graphene synthesis, researchers have exerted efforts to optimize the growth of bilayer graphene on Cu. However, limited to the self-terminating nature, the process has been found to impart higher growth speed to the top primary layer than to the bottom secondary layer of graphene. As Nie et al. have revealed, the secondary layer graphene nucleates and grows underneath the primary (or top) layer [151]. Consequently, the growth ceases when monolayer covers the entire Cu surface completely, leaving as low a bilayer-to-monolayer coverage ratio as a few percent. In addition, expansion of the secondary layer is often accompanied by the nucleation of the third layer, forming an inverted pyramidal configuration. To overcome these challenges, various growth techniques have been developed. Gan et al. have reported secondary layer expansion by carbon penetration through the fully covered “continuous” top-layer graphene [308]. Yet, this penetration mechanism is not necessarily correlated to high-quality continuous graphene. In addition, a Cu enclosure configuration (known as a Cu pocket) has been used to yield bilayer graphene on the outer side of the enclosure, attributed to the C bulk diffusion through the Cu foil [309-311]. However, this process is not always controllable, for it depends on how the Cu enclosure is prepared (often manually). Furthermore, bilayer graphene could be produced by manipulating the H$_2$ and carbonaceous precursor concentrations during CVD and/or Cu oxidation stage [312-315]. Other methods of growing bilayer graphene on Cu have been reported as well, such as an epitaxial deposition of carbonaceous fragments onto an existing graphene layer and a non-isothermal growth [316].

Despite the recent advancements, it is still challenging to produce high-quality AB-stacked bilayer graphene in a repeatable, scalable and
economic fashion. Most reports so far have focused on the phenomenological aspects of the bilayer growth. For the utilization of bilayer graphene in many applications, it is necessary to optimize the CVD process systematically and thus to attain selective bilayer growth (excluding of tri- and few-layer graphene) as well as a high binary-to-monolayer coverage ratio. Specifically, it is challenging to inhibit the rapid expansion of the primary graphene layer during the enlargement of the secondary layer underneath it. The formation of a continuous graphene top layer would isolate the underlying Cu catalyst from additional carbon supply, leading to growth termination of all the layers. Although desired, the task of suspending the expansion of the primary layer while enlarging the secondary layer is considered difficult because of the disproportional accessibility of each layer to of the available carbon precursor. Moreover, an active discussion on the kinetics of the secondary layer graphene on Cu remains far from completion. An in-depth understanding of the bilayer growth mechanism is crucial to provide guidance to the systematic optimization.

In order to attain the selective growth of the secondary layer of graphene as well as to better understand the underlying mechanism, here we design a growth-and-regrowth scheme, by which we show, for the first time, that the secondary layer regrowth follows the Gompertzian sigmoidal kinetics. With bolstering a postulate of a time-dependent transition of the secondary-layer expansion reaction from an early mass-transport-limited to a later lattice-attachment-limited regimes, our observations identify the mechanistic difference between the growths of the primary and the secondary layers. The selective expansion of the secondary layer is the result of a preferred diffusion of the reactant adsorbates crossing the edges of the primary layer, which could be engineered by tailoring the layer-edge-termination chemical states.

5.3.2 Results and Discussions

To promote the secondary layer expansion without allowing the primary (top) layer to cover the Cu surface completely, we conjoined two sequential processes of low-pressure CVD growth (Figure 5.3a). First, graphene flakes were grown with an annealing step (950 °C for 30 min, H₂ (20 sccm): Ar (1500 sccm) at total pressure of 3.6 mbar),
followed by short ethylene ($\text{C}_2\text{H}_4$) exposure. In this stage, graphene was synthesized as sparsely distributed individual flakes. Upon the primary layer growth, the graphene/Cu sample was cooled down, removed from the chamber into the ambient air and then reloaded into the chamber for sequential low-pressure CVD. At the annealing step of the regrowth process, we increased the $\text{H}_2$ partial pressure ($P_{\text{H}_2} = 0.23 \text{ mbar}$) so as to reduce and reactivate the oxidized Cu during the ambient air exposure. Upon this reduction annealing, the chamber temperature is rapidly increased to the growth temperature, before $\text{C}_2\text{H}_4$ was introduced for the secondary layer growth.

**Figure 5.3** Graphene regrowth method and the associated secondary-layer graphene expansion. (a) Schematic of the CVD regrowth method. (b) Representative SEM images showing that secondary layers expand selectively after the 2nd growth (regrowth). (c) Growth scheme and layer selection mechanism.

The bilayer area expanded predominantly during the regrowth as observed through scanning electron microscopy (SEM) imaging. After the first growth, each individual flake contains a small dark-contrast region at the center, corresponding to a bilayer seed, and a wide light-contrast region on the margin, corresponding to a single layer. The two layers share a common nucleation spot. After the regrowth, the bilayer area enlarges, while the overall flake size remains almost unchanged (Figure 5.3b). No new nucleation site is formed during the regrowth.
Newly attached C atoms extends the existing secondary layer. The sizes of both primary and secondary layers show quite uniform distributions across samples, indicating homogeneous growth conditions. Moreover, when the regrowth procedure was repeated in the absence of any carbon supply, neither the primary nor secondary layer expanded. This result suggests that the contribution from the remnant carbonaceous species, either dissolved in Cu or captured in the interspace between the primary graphene and Cu layers during the first growth, to the additional growth is unlikely or at least meager, and the continual expansion of the secondary layer is in fact sustained by the fresh carbon supply.

To explain the selective expansion of the secondary layer graphene during the regrowth, we designed a parametric study with various P_{H_2} and growth temperatures. First, we carried out a regrowth at a fixed temperature (950 °C) at different P_{H_2} (0.05 vs 0.23 mbar). We found out that the regrowth under P_{H_2} = 0.05 mbar yielded full covering of the sample by the primary layer with negligible expansion of the secondary layer, whereas P_{H_2} = 0.23 mbar resulted in the expansion of the secondary layer without any conspicuous change in the primary layer. This observation implies that the selective growth of the bilayer graphene is facilitated in a H_2-rich environment. Next, we fixed P_{H_2} at 0.23 mbar and ran the regrowth at 950 °C and 990 °C. At 950 °C, the secondary layer selectively expanded, while the primary layer area remained unchanged. At 990 °C, on the other hand, the layer expansion selectivity was switched in favor of the primary (top) layer; the primary layer expanded prominently, while the secondary-layer growth was negligible. Lastly, we evaluated the contribution of H_2-mediated graphene etching. Pre-grown graphene samples were exposed to P_{H_2} of 0.23 mbar and 950 °C. No pronounced etching of the pre-grown graphene was observed. Graphene etching was only notable in a very high P_{H_2} (>1 mbar) environment, far away from our parametric window and extremely uncharacteristic for standard growth recipes we conditioned for the C_2H_4 carbon feedstock. Therefore, the H_2-mediated graphene etching effect could be ruled out in this investigation, and the growth can be explained simply via reactant (carbon) kinetics at the copper surface. The conditions preferable for the selective secondary-layer expansion lie around P_{H_2}
of ~0.23 mbar and temperature of ~950 °C, according to our parametric characterization result.

A theory states that the edge state of a graphene lattice could be either “H-terminated” or “Cu-passivated”, depending on the $P_{H_2}$ and temperature of the CVD process and that this edge termination state determines the energy barrier for the C attachment onto the graphene lattice.[317] Accordingly, as illustrated in Figure 5.3c, for Cu-passivated edge, it is favorable for C adatoms to attach to the primary layer edge rather than to diffuse across the edge barrier into the area underneath the top layer; while the H-terminated edge will preferably usher the C adatoms underneath the top layer rather than being replaced by C termination. In our CVD condition of relatively high $P_{H_2}$ and temperature, the graphene edge of the primary layer would be H-terminated, inhibiting the primary layer expansion yet rather ushering the C adatom diffusion underneath itself to promote the secondary-layer expansion; in the meantime, $P_{H_2}$ underneath the primary layer would be much lower than that on the bare Cu surface, and thus the secondary layer graphene would most likely be Cu-passivated, preferably facilitating the C adatom attachment; consequently, the preferred lattice attachment on the secondary layer would disfavor the further C diffusion underneath to form the third layer. Altogether, a selective growth toward the secondary graphene layer is possible.

Raman spectroscopy can characterize the stacking order, layer number, and quality of the bilayer flakes. A central area of a flake (dark contrast, Figure 5.4b), before and after the regrowth, shows a Raman spectrum with an intensity ratio between $G'$ to G peaks of around a unity and a full width half maximum (FWHM) of the $G'$ peak of ~54 cm$^{-1}$ (Figure 5.4a). The $G'$ peak is asymmetrically shaped and decomposed to four Lorentzian peaks posing FWHM of ~30 cm$^{-1}$ each, indicating strongly an AB-stacked bilayer (Figure 5.4a inset). The deviation from a single Lorentzian $G'$ is explained by an electronic band splitting and an interlayer coupling of the bilayer graphene.[318, 319] The marginal region of a flake shows a Raman spectrum with a $G'$-to-G intensity ratio higher than 2, and the $G'$ peak fits well to a single Lorentzian function with FWHM of 33 cm$^{-1}$, indicative of a single layer (Figure 5.4b). The $G'$ peak center of the bilayer is blue-shifted in comparison to the single-layer area, which further confirms that the
center of the flake is an AB-stacked bilayer. Note that the D-to-G intensity ratio in the bilayer area is slightly higher than that in the single layer area, attributable to the defect-based nucleation, structural defects or additional grain boundaries.

**Figure 5.4** Quality of regrown bilayer graphene. (a-b) Raman spectra taken from the bilayer (a) and monolayer (b) areas of a graphene flake sample. Inset: 4-fold and single Lorentzian fits to the G’ peak (~2700 cm⁻¹). (c-f) Raman mapping of the bilayer graphene flakes for: (c) integrated area under the G’ band (2600-2800 cm⁻¹) (A_G’); (d) intensity ratio between G’ and G peaks (I_G’/I_G) normalized by the local maximum value of I_G/ I_G; (e) full-width-half-maximum of the G’ band (FWHM_G’); (f) integrated area under the D band (1300-1500 cm⁻¹) (A_D) normalized by the local maximum of A_D. (g-h) TEM characterization of the bilayer graphene: (g) a typical SAED pattern taken from the central bilayer area of a graphene flake, displaying a single set of diffraction patterns; (h) a corresponding intensity profile along the blue box of (g).
To further investigate the bilayer graphene flake after the regrowth, Raman maps of $A_G$ (integrated area under a G' band: 2600-2800 cm$^{-1}$), $I_{G'}/I_G$ (I for the intensity), full with half maximum of the G' peak (FWHM$_G$) and $A_D$ (integrated area under a D band: 1300-1500 cm$^{-1}$) are collected (Figure 5.4c-f). The maps display a clear contrast between single and bilayer areas. No observable defective boundary was detected at the edge of the flake. The defect density across the flake is rather uniform except very near the nucleation points, where $I_D$ rises, indicating dominant contribution from the defect initiated nucleation. The consistency of the AB-stacked bilayer before and after the regrowth confirms that the regrowth method preserves the original stacking order of the graphene.

Selected area electron diffraction (SAED) pattern is a reliable method to characterize the stacking order of the bilayer graphene. Because it can provide graphene with a global minimum potential energy surface, AB stacking is an energetically preferred configuration. By use of a 100-keV transmission electron microscope (TEM), we obtained SAED pattern for a graphene-transferred TEM grid. Diffraction pattern of a bilayer area of a typical regrowth graphene sample exhibited a single set of symmetric six-fold electron-diffraction pattern (Figure 5.4g). This pattern is a characteristic feature of the Bernal stacked bilayer, distinguishing from turbostratically stacked bilayer graphene, in which two sets of diffraction patterns should be observed. We also observed that the outer set of the diffraction pattern originating from equivalent planes (1-210) shows an intensity higher than that of the inner set of diffraction spots from equivalent planes (1-100) (Figure 5.4h). This feature indicates that the selected area is truly an AB-stacked bilayer rather than a single layer or a turbostratic bilayer.

In order to verify whether the AB stacking takes place at the nucleation stage or later at the expansion stage through a possible stacking reorganization process, we investigated the evolution of the stacking order of a double-layer graphene system (prepared by transferring the as-grown graphene monolayer on a SiO$_2$ substrate twice). Note that the van der Waals interaction between Cu and graphene is relatively weak (much weaker than the interaction of graphene with Ni and Fe) and that graphene grown on Cu is likely to reorient itself toward the thermodynamically favorable AB-stacking configuration.
Figure 5.5 Raman spectroscopy and TEM characterization of double layer graphene. (a-b) Raman spectra taken from the as-prepared double layer graphene before (a) and after (b) regrowth. Both (c-d) TEM characterization of the double layer graphene after regrowth: (c) a typical SAED pattern taken from the graphene flake, displaying two set of diffraction patterns; (d) a corresponding intensity profile along the blue box of (g).

For an arbitrarily stacked double layer of graphene, we expect turbostratic stacking in general. If a stacking self-reorganization process during the regrowth is active considerably, the AB-stacked configuration shall take over upon the regrowth. However, we observed that as-prepared double-layer graphene was turbostratic initially and continued to exhibit turbostratic SAED pattern after the regrowth at 950 °C for 30 min (Figure 5.5). Raman spectroscopy also represented a monolayer characteristic including single Lorentzian G' peaks for the double-layer graphene before and after the regrowth, indicating an unchanged turbostratic stacking configuration. Our observation does not support the significant self-reorganization between double graphene layers in the regrowth process. Hence, we
conclude that the stacking configuration taken at the initial nucleation stage is likely to preserve itself, attributable to energy optimization.

Figure 5.6 Scanning electron micrographs of the bilayer flakes regrown at various CVD temperatures and times, with no change in the size of the primary layer.

Next, we further elucidate the kinetics and associated mechanisms of the regrowth responsible for the selective growth. We statistically determined the time-dependent flake sizes of both primary and secondary layers of graphene by averaging 100 random flake sizes of each sample and repeating it for various regrowth durations and temperatures (Figure 5.6, Figure 5.7). The primary layer area remains unchanged upon regrowth. The secondary layer expansion could be rationalized by a Gompertz function of the form:

\[
A(t) = A_{\text{max}} \exp \left\{ -\exp \left[ -\frac{\mu_m e}{A_{\text{max}}} (t - \lambda) + 1 \right] \right\},
\]

where \(A\) is the area of the secondary graphene flake (\(\mu m^2\)), \(A_{\text{max}}\) is the maximum area of secondary graphene flake (\(\mu m^2\)) at the growth saturation, \(\mu_m\) is the maximum growth rate (\(dA/dt\) at the inflection
point), $e$ is Euler's number, $\lambda$ is the time lag (min) measured by the abscissa intersection of the tangent drawn from the inflection point, and $t$ is the growth time (min). The recursive least squares ($R^2$) was $>0.98$ throughout the analyses.

![Image](image-url)

**Figure 5.7** (a) Schematics of the graphene growth mechanism and the associated energy profile for the surface diffusion and lattice attachment of C adatoms in a H-terminated top-layer edge. (b) Evolution of the average sizes of the top primary layer and the underneath secondary layer graphene as a function of time.

A few observations are crucial to understand the underlying secondary-layer expansion kinetics. First, the secondary layer extends at an initially increasing speed. This observation rules out the possibility of supersaturation as a major carbon supply for the secondary-layer expansion. If the carbon supply for the secondary layer is from pre-dissolved C in Cu bulk or in defects of a Cu foil, the growth rate would decrease monotonically. Our data of the initially increasing growth rate indicate that the expansion of the secondary layer is an outcome of continuous carbon supply. Second, the secondary-layer expansion eventually reaches saturation, suggesting that the maximum areal coverage is finitely determined given the carbon precursor supply and the thermodynamic CVD condition. Moreover, we note a time shift of the inflection point toward an earlier moment as temperature increases. It is known that an appearance of the inflection point in the Gompertzian kinetics hints a competition between two opposing mechanisms in the growth. For the monolayer graphene growth, the competition has been proposed to be between the Cu-sublimation-promoted desorption of C adatoms and intermediate species and the dissociative dehydrogenation of C$_2$H$_4$-[153]. The higher
the temperature, the more enhanced the Cu sublimation with extending the incubation period to a later moment. Interestingly, the kinetic trend we observed here for the secondary-layer expansion is opposite to that for the monolayer, likely associated with a new Cu environment covered with the primary layer. Providing that the primary flake area is constant during the regrowth, the amount of the uncovered Cu area and the related Cu sublimation are ought to be unchanged. Besides, the growth of the secondary layer takes place underneath the primary layer, where Cu sublimation is basically negligible. At high temperatures, dissociation and dehydration as well as surface diffusion of C adatoms are all likely to be active. Thus, the fast formation and transport of C adatoms can facilitate their entrance to the narrowly confined two-dimensional channels, or interspace, in between the primary layer and the underneath Cu surface. As the result, shortened incubation at increased temperature is justified for the secondary-layer growth.

Figure 5.8 Quantitative kinetics of the secondary-layer expansion. (a) Gompertzian kinetics for various growth temperatures. (b) Secondary-layer expansion rate as a function of inflection-point-normalized time. (c)
Time-variant activation energy ($E_A$). Inset: an Arrhenius plot of the inflection-point growth rate, $\mu_m$ ($\mu$m$^2$/min), of the secondary layer, yielding $E_A$ of 1.4 eV. (d) Fitting of the equilibrium reaction model for the temperature-reliant saturation area of the secondary layer to the experimental data ($\theta_c$), revealing $\Delta H_1 + \Delta H_2$ of 0.98 eV in great agreement (within 5%) with DFT calculation.[317, 320]

The above mechanism was further investigated by quantifying the dispersive kinetics and the associated energetics of the graphene regrowth in a time-temperature parametric window. To extract information pertaining to the activation energy pathways, the evolving secondary layers were monitored over a growth time ($t$) window of 7-60 min and a temperature window of 890-970 °C (Figure 5.8a, Figure 5.6). The growth rate at each regrowth temperature was evaluated as a function of inflection-point-normalized time ($t/\tau$), in order to correspond the temperature-dependent growth rate to the rate of the equivalent secondary-layer formation reaction (Figure 5.8b). The corresponding activation energies ($E_A$) can be obtained as a function of the normalized time. Time-variant $E_A$ is known to be associated with dispersive reaction kinetics [153]. The overall ensemble-averaged $E_A$ decreases with time to a minimum value of 1.4 eV (Figure 5.8c) and then increases as the growth slows down toward saturation. $E_A$ at the inflection point ($t = \tau$) is often used to characterize the rate limiting step in the Gompertzian kinetics, since it represents the turning point of the slope of the curve from positive to negative and is an inherent property of the cascade reactions responsible for the dispersive kinetics. At $t < 0.2\tau$ the Arrhenius plot is highly nonlinear (Figure 5.9), which implies that the secondary-layer expansion reaction lies in a mass-transfer-limited growth regime rather than in a reaction-limited one. The plots take linearity as the growth proceeds ($0.5\tau < t < 5\tau$), suggesting the chemical-reaction-limited regrowth. After $5\tau$, the growth rate becomes negligibly small due to the growth saturation, nullifying the Arrhenius analysis.

To identify the rate limiting step using $E_A$, we account for the processes discussed above: a) hydrocarbon adsorption on Cu; b) surface diffusion on the bare Cu or the graphene-coved area; c) catalytic dissociation/dehydrogenation into various intermediates and C adatoms; d) surface diffusion across the primary-layer edge; and e) graphene lattice construction for the secondary-layer expansion. It is
unlikely that the process is limited by surface diffusion on the bare Cu or the graphene-coved area, for its energy barrier lies below 0.5 eV. The C\textsubscript{2}H\textsubscript{4} adsorption is also unlikely to limit the reaction because of its small \(E_A\) (<0.1 eV). In the case of the catalytically dissociative dehydrogenation of C\textsubscript{2}H\textsubscript{4} on Cu, the energy barrier (>2 eV) is rather much higher than our measurement (1.4 eV). The energy barrier for the lattice attachment of C adatoms (1-2 eV) seems finally to fall in the common \(E_A\) range of our measurement.

**Figure 5.9** Arrhenius plots of the secondary-layer expansion rate (\(dA/dt\) in \(\mu m^2/min^2\) in a natural log scale) at various time scales, \(t/\tau\), of 0.2 (red), 0.5 (green), 1.0 (blue), and 5.0 (orange), showing deviation from the reaction-limited regime at the very early stage of the regrowth \((t/\tau = 0.2)\).

We have speculated in the earlier discussion that the two competing mechanisms participating in the secondary-layer regrowth to be the dissociation/dehydrogenation of C\textsubscript{2}H\textsubscript{4} and the lattice attachment. According to one first principle calculation, C monomer is the dominant active species for the secondary-layer growth, as it is most likely to diffuse underneath the top (primary) layer [317]. Species such as C\textsubscript{2} and C\textsubscript{x}H\textsubscript{y} have significantly larger formation energy difference on the Cu surface underneath the graphene cover as compared with on the
uncovered Cu, stemming from the energy required for C₂ and CₓHᵧ species to diffuse underneath the graphene layer. As a result, a huge concentration drop underneath the graphene cover is expected. Based on the above discussion, we can draw a kinetic picture of the secondary-layer regrowth process. As C₂H₄ approaches a graphene flake sample on a Cu substrate during the regrowth, it adsorbs onto the bare Cu area; under our CVD condition, graphene is catalytically inactive, ruling out direct carbon deposition on it. Subsequently, the adsorbed C₂H₄ either desorbs from the catalyst or enters into catalytic decomposition and dehydrogenation. The formation of C adatoms requires full decomposition and dehydrogenation of C₂H₄. For our CVD temperatures, the remaining reactants on Cu are expected to decompose and dehydrogenate into a mixture of C adatoms, dimers, and intermediate hydrocarbon species, which can spontaneously go through additional surface reactions until lattice attachment or desorption occurs. Depending on the detailed constituents, these species are free to diffuse around the bare Cu surface with a relatively low energy barrier. In diffusing underneath the primary layer and conducing to the secondary-layer expansion, C adatoms encounter another energy barrier depending on the termination status (H-terminated or Cu-passivated) of the primary-layer edge. When the edge is H-terminated, the approaching C adatoms could preferably diffuse underneath the layer across the edge. It is the process of decomposition and dehydrogenation of C₂H₄ to C adatoms required in the prior state that leads to the low yet increasing expansion rate of the secondary-layer expansion during the initial phase. With time, C adatoms amass on the uncovered Cu surface and diffuse underneath the primary layer until the supply reaches the demand at the inflection point. Afterwards, lattice attachment becomes the rate-limiting step for the secondary-layer expansion. In the meantime, as C monomers diffuse underneath the primary graphene layer, so do H atoms. C and H atoms have to compete for the edges of the secondary graphene layer. The lattice attachment rate of C adatoms slows down as the finite number of Cu catalytic sites underneath the primary layer are increasingly occupied by H adatoms. Eventually, the growth reaches saturation when the edges of the secondary layer are predominantly H-terminated. Preference of the secondary-layer edge termination is a function of temperature that results in the temperature-reliant saturation area of the bilayer flake.
Indeed, our kinetics data shows that the saturation area of the bilayer graphene is a function of temperature. Saturation usually occurs after a long period of time, around 30 mins, after which the secondary layers do not expand any longer. Postulating that it is the continuous carbon supply rather than initially captured carbon amount that drives the secondary-layer expansion, we construct a model for the saturation size of the secondary layer in the regrowth process. We first define the primary-layer-covered area to be a domain $D_1$, the secondary-layer-covered area as $D_2$, and a subdomain $D = D_1 - D_2$. The domain $D_1$ has a fixed area during the regrowth because the primary layer does not expand or is not etched away. Therefore, the outer domain area, which is the bare Cu surface, is also fixed. We model the overall regrowth reaction into three individual reversible reactions:

$$C_{\infty} + S_D \leftrightarrow C_D \quad (5.2)$$

$$H_{\infty} + S_D \leftrightarrow H_D \quad (5.3)$$

$$C_D + S_{Gr} \leftrightarrow \text{graphene} \quad (5.4)$$

where $C_{\infty}$ and $H_{\infty}$ are the areal concentrations of the C and H adatoms entering the domain D, respectively, $S_D$ stands for the catalytically active Cu sites unoccupied by C or H yet, $C_D$ and $H_D$ are the areal concentrations of the adsorbed C and H within the subdomain D, and the “graphene” within the domain $D$ stands for the secondary layer graphene per unit area. We assume that C and H adatoms bind competitively to the available surface sites of Cu uncovered with graphene. $S_{Gr}$ is the graphene edge sites participating in C attachment. As the C attachment on the edge of H-terminated graphene is much harder than on C-terminated graphene (energy barrier of 1.67 eV vs 0.71 eV, respectively) [317], we assume that the graphene edge site turns inactive for additional C attachment once it is terminated by H. Note that the detachment of C from the C-terminated edge sites is easier than C detachment from H-terminated edge (1.33 eV vs 1.67 eV). At the saturation state, the overall graphene edge sites are terminated by H or C. The H-terminated edges are inactive for further graphene expansion, and the C-terminated edges lie in equilibrium between C attachment and detachment.
We can express the rate of the D-entering ($r_{+1}$) and leaving ($r_{-1}$) C adatoms to be $r_{+1} = k_{+1} C_{\infty} S_D$ and $r_{-1} = k_{-1} C_D$, respectively. Then, the surface concentration of C and H can be expressed as $C_D (1 - \theta_{Gr}) = \rho_s \theta_C$, and $H_D (1 - \theta_{Gr}) = \rho_s \theta_H$, where $\rho_s$ is the areal density of the surface sites on Cu, and $\theta_C$, $\theta_H$, $\theta_{Gr}$ are the fractional coverage of C, H, and graphene, respectively. $S_D$ is related to the fractional coverage of the vacant sites within D, $\theta_s$, as $S_D = \rho_s \theta_s$. The fractional coverages satisfy $\theta_C + \theta_H + \theta_{Gr} + \theta_s = 1$.

At equilibrium, we define the equilibrium constant $K_1 = k_{+1} / k_{-1}$ for reaction (5.2) as

$$K_1 = \frac{C_D}{C_{\infty} S_D} \frac{\theta_C}{(1 - \theta_{Gr}) \theta_C} = A_1 \exp \left[ -\frac{\Delta H_1}{k_B T} \right],$$

(5.5)

where $\Delta H$ and $k_B$ are the activation energy and Boltzmann constant, respectively. Similarly, for the domain-entering H, $r_{+2} = k_{+2} H_{\infty} \rho_s \theta_s$ and $r_{-2} = k_{-2} H_D$, respectively, and the corresponding equilibrium constant, $K_2$, is

$$K_2 = \frac{H_D}{H_{\infty} S_D} \frac{\theta_H}{(1 - \theta_{Gr}) \theta_H} = A_2 \exp \left[ -\frac{\Delta H_2}{k_B T} \right].$$

(5.6)

Finally, for the graphene formation step, we consider the balance between attachment ($r_{+3} = k_{+3} C_D S_{Gr}$) and detachment ($r_{-3} = k_{-3} S_{Gr}$) of C adatoms to obtain the corresponding equilibrium constant, $K_3$:

$$K_3 = \frac{1}{C_D} \frac{1 - \theta_{Gr}}{\rho_s \theta_C} = A_3 \exp \left[ -\frac{\Delta H_3}{k_B T} \right].$$

(5.7)

Solving for the graphene coverage, we obtain

$$\theta_{Gr} = 1 - \frac{1}{K_1 K_3 C_{\infty} \rho_s} \left( 1 - \frac{1}{K_3 \rho_s} - \frac{K_3 H_{\infty}}{K_1 K_3 C_{\infty} \rho_s} \right)^{-1}.$$

(5.8)
Under a typical CVD condition where partial pressures of $\text{C}_2\text{H}_4$ and $\text{H}_2$ are below 1 MPa, and temperature is lower than 1300 K, we assume $\theta_S >> \theta_C, \theta_H$, and thus

$$\theta_{Gr} \approx 1 - \frac{1}{K_1K_3\rho_{Gr}} = 1 - A \exp \left( \frac{\Delta H_1 + \Delta H_3}{k_B T} \right),$$

(5.9)

$$\ln(1 - \theta_{Gr}) = \left[ \frac{\Delta H_1 + \Delta H_3}{k_B T} \right] + \text{const.}.$$  

(5.10)

Using eq. (5.10) for the bilayer graphene coverage within the domain $D$ as a function of temperature, we can fit the experimentally data of the secondary flake area. The result is that $\Delta H_1 + \Delta H_3 = -0.98$ eV (Figure 5.8d). From DFT calculations, we can estimate that the enthalpy for C adatoms to diffuse underneath the H-terminated primary-layer edge is -0.32 eV [320] and the enthalpy of graphene formation is about -0.71 eV [317], altogether yielding a theoretical prediction of $\Delta H_1 + \Delta H_3 = -1.03$ eV, which agrees with our data within 5%.

The temperature-reliant saturation behavior of the secondary-layer regrowth kinetics could be supported well by the model of competitive attachment of C and H on the secondary-layer graphene edge. High temperatures promote C adatoms to diffuse underneath the primary layer and attach rapidly on the secondary-layer edge (reactions (5.2) and (5.4)); yet they also accelerate the H termination of the graphene edge leading to early termination (saturation) of the secondary-layer expansion. In contrast, low temperatures decelerate both the C attachment and the H termination on the graphene edge. Overall, the impact of the CVD temperature on the C attachment rate outweighs that on the H termination, resulting in a positive correlation between the regrowth temperature and the saturation area of the regrown bilayer flake.

Compared with the monolayer graphene growth on Cu, our secondary-layer regrowth mechanism exhibits a few clear disparities. First, growths of the primary and the secondary layers take distinct time
scales. The growth time scale for the secondary-layer regrowth is one-order-of-magnitude larger than that for the primary-layer growth. Second, \( E_A \) at the inflection point of the secondary-layer expansion is much lower than that of the monolayer growth. A typical value for the monolayer growth is around 3 eV \([153]\), which revokes \( \text{C}_2\text{H}_4 \) dissociation and dehydrogenation. The much longer time scale and lower activation energy of the secondary-layer expansion kinetics suggest disparate rate-limiting mechanisms between the monolayer growth and the secondary-layer expansion underneath the primary-layer cover. In the bilayer regrowth mechanism, there is an extra energy barrier for the reactants to overcome in association with the penetration across the primary layer edge. This edge-state-related barrier can usher in \( \text{C} \) adatoms selectively among other (intermediate) species, thereby inducing the layer-selective growth. If combined with an initial insufficient amount of adsorbed reactants outside the primary layer cover, this barrier could also be co-responsible for a sluggish supply of \( \text{C} \) adatoms at the very early stage of the secondary-layer regrowth, manifested by the appearance of a mass-transport-limited reaction regime at this stage.

5.3.3 Experimental Methods

All graphene growth and regrowth were carried out in a commercial, cold-wall CVD reactor (Black Magic\textsuperscript{TM}, AIXTRON, Ltd.). After cleaning the chamber with \( \text{H}_2 \) exposure at high temperature, Cu foils (99.8\% purity, Alfa Aesar) were first loaded on the sample stage, 41 mm below the gas shower head, and the chamber was evacuated to sub-0.2 mbar. The sample stage was then heated up to 950 °C at 200 °C/min and remained at 950 °C and 3.6 mbar for 30 min under a flow of 20 sccm of \( \text{H}_2 \) (99.999\%) diluted with 1500 sccm of \( \text{Ar} \) (99.999\%). After the annealing, the first growth began with adding 5 sccm of \( \text{C}_2\text{H}_4 \) for 45 s to the reductant gas (\( \text{H}_2 \)) flow. The \( \text{C}_2\text{H}_4 \) exposure time during the first growth was chosen to yield individual flakes having suitable size and density for the subsequent regrowth. The chamber was cooled down immediately upon stopping the \( \text{C}_2\text{H}_4 \) flow. In order to prevent Cu oxidation during the cooling caused possibly by a trace amount of \( \text{O}_2 \) present in the chamber, the reductant gas flow was maintained until the sample temperature reaches <400 °C. At the sample stage temperature below 100 °C, graphene samples were taken out into
ambient air for characterization. Later, the samples were reloaded into the chamber for the regrowth. During the regrowth, various H\textsubscript{2} partial pressures (P\textsubscript{H\textsubscript{2}}) and annealing durations were tested. For the selective bilayer growth, the samples were annealed at 950 °C under 100 sccm of H\textsubscript{2}, diluted again with 1500 sccm of Ar (99.999%) for 15 min. Parametric investigation of the secondary-layer expansion was carried out under one consistent annealing condition for all CVD runs to ensure that all growths initiate at the similar edge-termination states and at the comparable Cu grain sizes. The C\textsubscript{2}H\textsubscript{4} partial pressure (P\textsubscript{C\textsubscript{2}H\textsubscript{4}}) and the total chamber pressure for the regrowth were identical as those of the first growth.

As for the potential etching effect of H\textsubscript{2}, control experiments were carried out to verify that 100 sccm of H\textsubscript{2} during the cooling process did not induce observable differences in the graphene flake size. This observation suggests that there is negligible etching of graphene, in association with atomic H, for low P\textsubscript{H\textsubscript{2}} (< 0.05 mbar) and temperatures (< 900 °C).

The gas residence time was calculated to be far shorter than 1 s, preventing C\textsubscript{2}H\textsubscript{4} from undergoing any significant gas-phase thermal rearrangement. Our in-situ quadruple mass-spectroscopy under the described growth conditions confirmed that the single prevalent carbon feedstock species impinging the Cu surface is C\textsubscript{2}H\textsubscript{4} in the presence of Ar, H\textsubscript{2}, and a trace amount of moisture.

For the Raman spectroscopy characterization, as-grown graphene films on Cu were first transferred onto a SiO\textsubscript{2} substrate and then characterized by micro Raman spectroscopy (In-Via, Renishaw, Ltd.) with 457 nm and 532 nm excitation wavelengths at an incident power of 2 mW. The focal spot size for each excitation wavelength is approximately 0.6 μm and 1.2 μm, respectively. SAED was performed with TEM (Philips CM 12 at 100 keV) after transferring graphene onto a lacey carbon TEM grid (400 copper mesh, TED Pella). Surface morphology was characterized using a field emission SEM (Nano500, FEI) operated at 1 kV. The average graphene flake sizes were determined out of the measurements of about 100 flakes. Origin Pro 9 software is used for the data analysis and the curve fittings.
5.4 Conclusion

Today, CVD on Cu has become the most convenient and popular synthesis method to produce high-quality graphene. Unlike other transition metals, Cu does not dissolve carbon very much in bulk and thus supports, under the correct growth conditions, the self-limiting growth of monolayer graphene with insignificant wrinkling and rippling. Advances in the understanding of the fundamental growth mechanisms have permitted the synthesis of the high-quality polycrystalline graphene with larger and better-connected grains. Compared with the monolayer graphene growth mechanism on Cu, our analysis on secondary layer affirms that the chemical state of the graphene edge plays a critical role in the synthesis of AB-stacked bilayer graphene. The growth-and-regrowth method enables in part the size-controlled growth of the bilayer graphene by rendering the edge of the top primary layer H-terminated and that of the underneath, primary-layer-covered one Cu-passivated; in this way, one can allow an optimal expansion of the secondary layer with holding the size of the primary layer. The Gompertzian kinetics of the secondary-layer expansion is observed as an outcome of both the dissociation/dehydrogenation of C2H4 into C adatoms (at an initial stage of the CVD process) and the C-adatom attachment to the extending lattice of the secondary layer (after the inflection point). When the growth comes to saturation, the temperature-reliant area of the bilayer graphene is resulted from the competitive attachment of C and H adatoms onto the secondary-layer edge. Our investigation can offer insights into the layer-selective synthesis of AB-stacked bilayer graphene as well as provide guidance for the CVD process optimization. Strategies to manipulate the edge state of the primary layer graphene and the activities of the adsorbed reactants could be established in order to promote the dissociation/dehydrogenation of the carbon feedstock, the diffusion of C adatoms underneath the primary layer, their attachment to the secondary-layer edge, and consequently the growth efficacy of the bilayer graphene flakes.
6 Epilogue

The controlled CVD synthesis of low dimensional materials, VA-CNT and bilayer graphene in particular, has been investigated in this thesis.

VA-CNTs pose an excellent opportunity stemming from the properties of one-dimensional graphitic nanotubes, individual and collective, which opens new avenues to the carbon nanotube applications. To fulfill the demands of various target applications, much of the current research has been focusing on the efficient and controlled synthesis of the CNT forests, understanding and tailoring many aspects of the growth and characterizing the properties of the resultant structures. We carried out systematic studies in a TG-CVD setup. The TG-CVD approach we take bases its unique controllability on the use of dual heaters that can generate temperature gradient in the carbon precursor gas mixture between gas injector and catalysts. Various thermal environments are provided for the reaction of carbon feedstock (e.g., acetylene) in the chamber, resulting in different combinations of active carbonaceous reactant species atop the catalyst. We observe that the activation energy deviates from the original value, corresponding to a growth with no precursor thermal rearrangement, to higher values at increased acetylene partial pressure and acetylene pre-treatment temperature. We correlate the deviation with cumulative effect of the secondary pyrolysis products and propose a parallel reaction model in conjunction with the Eley-Rideal mechanism. We propose an analytical model with multiple reaction pathways, which takes into account the cumulative effect of the secondary acetylene-pyrolysis products on the surface reaction of CNT growth. Our simulation results based on the proposed mechanism agree well with our experimental data that do not allow for an explanation by single-rate-limiting-step based kinetic models. Our work unveiled complex catalysis of the CVD process. Obtained data and simulation results will allow us to create new knowledge on the diameter-selective VA-CNT growth via the single-chamber TG-CVD. Moreover, growth of VA-CNTs having sub-1.5-nm diameters is demonstrated by optimizing the interaction between catalyst and support. The alumina support is engineered via a sequential process: heat treatment followed by ion beam bombardment. The order of the alumina treatments is found out to be
critical to the growth efficiency and the narrow distribution of the tiny CNT diameters. Supported by microscopic and spectroscopic evidence, we scrutinize the influence of the alumina surface properties on the evolution of catalysts and hence postulate the positive contribution of alumina to the diameter-controlled growth of CNTs upon acquiring distinctive surface and bulk properties.

Next, high-quality mono- and bilayer graphene growth by ethylene precursors has been studied. For monolayer graphene, the resulting continuous graphene is shown to cover over 98.4% of the Cu foil area, with the remaining occupied largely by bilayer. The fundamental mechanism that governs the kinetics of the CVD growth of graphene is found as the catalytic dissociative dehydration of $\text{C}_2\text{H}_2$ on Cu surface. Cu sublimation is found to hinder the growth by enhancing desorption of carbonaceous species from the surface. For the bilayer graphene, we report a systematic investigation on the kinetics and termination mechanisms of bilayer graphene on Cu using a regrowth method. In this regrowth method, the secondary graphene layers already nucleated along with primary layers enlarge selectively, whereas enlargement of the primary layer is inhibited, ascribed to the oxidation of the nearby Cu surface as well as to the H-termination of the primary flake edge. We allocate the edge termination state of the top primary layer graphene as the key parameter for this layer selective growth. A reaction mechanism based on the surface diffusion of H and C adatoms as well as C-to-graphene incorporation describes the saturation behavior of the secondary layer graphene growth. The growth limiting step seems to change with time, exhibiting a transition from diffusion-limited to reaction-limited regimes.


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Curriculum Vitae

Name: Ning Yang

Date of Birth: May 8\textsuperscript{th}, 1991

Place of Birth: JiangXi, China

Nationality: Chinese

08/12-01/17 PhD Candidate in Engineering
Nanoscience for Energy Technology & Sustainability, Institute of Energy Technology, Department of Mechanical and Process Engineering, ETH Zurich, Switzerland
Supervisor: Prof. Hyung Gyu Park

06/10-06/12 Master’s Thesis in Electrical Engineering
NanoLab, Ming Hsieh Department of Electrical Engineering, University of Southern California, United States of America
Supervisor: Prof. Chongwu Zhou

09/06-06/10 Undergraduate Study in Electrical Engineering
Nanjing University of Science and Technology, Nanjing, China
Publications and Conferences