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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SYNTHESIS AND CHARACTERIZATION OF
LOW DIMENSIONAL CARBON MATERIALS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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SYNTHESIS AND CHARACTERIZATION OF LOW DIMENSIONAL CARBON MATERIALS

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ABSTRACT

This thesis presents the research works on synthesis and characterization of low dimensional carbon materials, including single-walled carbon nanotubes (SWNTs), *sp* hybridized carbon chain (C_n) and SWNT hybrid system, single layer graphene, bilayer graphene, nitrogen doped graphene, and hydrogenated graphene.

Synthesis of high quality vertically aligned SWNTs by plasma enhanced chemical vapor deposition was achieved at low temperature (500 °C). For low temperature synthesis of SWNTs, both aggressive ion bombardment in discharge sheath and large C_2H_4/H_2 flow rate ratio can lead a structural transition from SWNTs to few-walled carbon nanotubes. In capacitively coupled radio frequency plasma, the ion flux, which is significantly dependent on the plasma powers and pressures, was found to be the determinant factor of the ion bombardment etching effect.

With low density radio frequency plasma and special Co-Fe catalyst, linear carbon chains encapsulated in SWNTs, $C_n@SWNTs$, were synthesized for the first time. The *sp* hybridized linear carbon chains were identified by resonant Raman spectroscopy and high resolution transmission electron microscopy. The charge transfer between carbon chains and SWNT make this unique hybrid system a novel one dimensional metal with Luttinger-liquid behavior.

Single layer graphene and bilayer graphene were synthesized homogeneously in a controllable manner by low pressure chemical vapor deposition. The electronic structures of bilayer graphene were characterized by Raman spectroscopy, photoelectron spectroscopy and optical absorption spectroscopy, and carrier dynamics in bilayer graphene was probed by transient absorption spectroscopy. The results of all these studies

imply that the stacking order in bilayer graphene is close to AB stacking and the electronic bands near K point are in split form.

Nitrogen-doped single layer graphene incorporated with N percentage up to 16% was synthesized in presence of NH_3 . The structural and chemical imaging of nitrogen-doped single layer graphene showed that the distribution of incorporated N in graphene was in domains with size of 1~2 μm . The electronic structure characterization revealed that the N-C bonding configuration was pure pyridinic N. The single layer graphene incorporated pure pyridinic N offers an excellent platform for studying doping effect of pyridinic N on the physical and chemical properties of carbon materials.

Hydrogenated graphene was studied intensively as a case study of graphene derivatives. An ionic hydrogenation process via H_2 plasma was developed for hydrogenation of graphene. Both the hydrogenation and dehydrogenation of graphene layers show thickness dependent energy barriers. The evolution of structures and electronic structures of single layer graphene with different amounts of hydrogen coverage was investigated by Raman spectroscopy, photoelectron spectroscopy and optical absorption spectroscopy. A band gap opening was observed at high hydrogen coverage. In Raman spectroscopy study, excitation energy dependent saturation effect on the ratio of integrated intensities of D and G Raman bands (I_D/I_G) was revealed and a D band Raman active model with both D band Raman relaxation length and photo-excited electron/hole wavelength as critical length scales was developed for interpretation of this phenomenon.

Chapter 1

Introduction

1.1 Introduction to graphene

Graphene is a two-dimensional crystal made of carbon atoms arranged in a honeycomb lattice [1]. The lattice structure of graphene is shown in Figure 1.1. There are two dissimilar carbon atoms A and B in a unit cell of graphene. The unit cell vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ can be written as,

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}), \quad \mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3}), \quad (1.1)$$

where $a \approx 1.42 \text{ \AA}$ is the distance between two adjacent carbon atoms [1]. The calculated reciprocal lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ can be expressed as,

$$\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad \mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \quad (1.2)$$

Figure 1.1. Lattice structure of graphene (left) and its Brillouin zone (right). The Γ , M , K and K' are high symmetry points in Brillouin zone. Adapted from Castro Neto et al.[1].

The energy bands of graphene can be derived from tight banding approach [1].

$$E_{\pm}(k) = \pm t \sqrt{3 + f(k)} - t' f(k) \quad (1.3)$$

$$f(k) = 2 \cos(\sqrt{3} k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2} k_y a\right) \cos\left(\frac{3}{2} k_x a\right) \quad (1.4)$$

where t is the nearest-neighbor hopping energy and t' is the next nearest-neighbor hopping energy. A linearly dispersion can be obtained by expanding electronic band dispersions around $K(K')$ point, where $|q|$ is much smaller than $|K(K')|$.

$$E_{\pm}(q) \approx \pm v_F |q| + O\left[(q/K)^2\right] \quad (1.5)$$

where q is electron momentum measured from $K(K')$ point and v_F is Fermi velocity given

by $v_F = \frac{3ta}{2}$ with a value of $\sim 1.0 \times 10^6$ m/s [1]. Figure 1.2 displays the electronic

structures of graphene with $t = 2.7$ eV and $t' = -0.2t$. A linearly dispersion of electronic band structures located around $K(K')$ point is shown in the enlargement.

Figure 1.2. Left: Electronic band structures of graphene (E_k is in units of t). Right: The zoom in image of band structure around $K(K')$ point. Adapted from Castro Neto et al.[1].

The linear dispersion located at the corner of the Brillouin zone leads to fascinating electronic and optical properties in graphene, such as anomalous quantum Hall effect, Klein tunneling, valley polarization, ultrahigh carrier mobility, universal optical conductivity, as well as saturate optical absorption [1-6]. These unusual physics properties of graphene make it a promising candidate for fabrication of novel electronic and photonic devices. Detailed information about the physics properties and potential application of graphene could be found in some excellent review articles [1-6].

Beside the graphene, bi-layer graphene (BLG), a system of two stacked monolayer graphene, also shows fascinating physics properties according to its unique atomic and electronic structures [1,7,8]. The most energetically preferred stacking order of BLG is AB (Bernal) stacking, where a carbon atom in one layer is in the center of the other layer's hexagon [1]. AB stacking can be described by Slonczewski-Weiss-McClure model with SWM parameters in term of γ_0 , γ_1 , γ_3 , and γ_4 . As indicated in Figure 1.3, $\gamma_0 = t$ is the in-plane hopping energy, $\gamma_1 = 0.3$ eV is the hopping energy between atom A1 and atom A2, $\gamma_3 = 0.1$ eV is the hopping energy between atom B1 and atom B2, $\gamma_4 = 0.12$ eV is the hopping energy between atom A1 and atom B2 [1, 9].

In tight-binding description, the low energy electronic structures of AB stacked BLG can be described by the following energy dispersion relation [1]:

$$E_{\pm}(q) = [V^2 + \hbar^2 v_F^2 q^2 + t_{\perp}^2 / 2 \pm (4V^2 \hbar^2 v_F^2 q^2 + t^2 \hbar^2 v_F^2 q^2 + t_{\perp}^4 / 4)]^{1/2} \quad (1.6)$$

where t , v_F are the intra-layer hopping energy and graphene Fermi velocity for monolayer graphene, and $t_{\perp} = \gamma_1$ is the interlayer hopping energy. The quantity V corresponds to the possibility of a shift in the electrochemical potential between the two layers, which would induce an band gap opening near the $K(K')$ point. Figure 1.4 shows electronic band

structures of BLG in AB stacking, in which the energy dispersion follows a hyperbolic dispersion and splits into two parabolic branches. The possible existence of an external bias-induced band gap between the conduction and valence band and the parabolic dispersion around $K(K')$ point distinguish BLG from monolayer graphene [1,10].

Figure 1.3. Atomic structure of BLG in Bernal stacking as well as Slonczewski-Weiss-McClure (SWM) parameters associated with different hopping processes. Adapted from Castro Neto et al.[1].

Figure 1.4. (a) Electronic band structures of BLG in the absence of an external electric field. (b) Electronic band structure of BLG near the K point for $U_{\text{ext}} = 0, 0.5$, and 1 eV. Adapted from Min et al.[10].

1.2 Introduction to graphene derivatives

If we consider the graphene as a giant flat molecule, attaching exotic atoms or functional groups, such as H, F, O, and OH, on the carbon scaffold of graphene can convert graphene into new giant molecules, so called graphene derivatives [11-13]. These graphene derivatives, as new two dimensional crystals, possess distinct electronic structures and different electrical, optical, and chemical properties. A well known example of graphene derivatives is graphane [14], a highly stable two dimensional hydrocarbon with one hydrogen atom attached to every carbon atoms on alternating sides of the graphene plane for adjacent carbon atoms, as illustrated in Figure 1.5.

Figure 1.5. The structure of graphene (left) and graphane (right). Adapted from Novoselov et al. [13].

Since the π -electrons are bound to hydrogen atoms, all of the carbon atoms are in sp^3 hybridization, resulting in the absence of free π electrons in the hexagonal network. Density functional theory (DFT) calculation of the electronic band structures of graphane

indicated it was an insulator with a large band gap (~ 3.5 eV) [14]. Interestingly, when only one side of graphene was attached with H atoms, the resulted half-hydrogenated graphene (see Figure 1.6), which is called graphone, is also a stable graphene derivatives [15]. Half-hydrogenation breaks the delocalized π bonding network of graphene, leaving the electrons in the H free carbon atoms localized and unpaired. The magnetic moments in H free carbon atoms can couple each other ferromagnetically, and therefore graphone becomes a novel ferromagnetic semiconductor with a small band gap [15].

Figure 1.6. Atomic structure of graphone (left) and its side view showings C-C and C-H distances (right). Adapted from Zhou et al. [15].

Graphene derivatives fabricated by chemical surface modification offer a simple way to control the electronic structures, which is of great interest for many applications in nanoelectronics. Traditional circuit fabrication involves cutting or etching the graphene into a particular shape or size. In contrast, selective chemical modification of graphene surface has been proposed as an easier alternative way to fabricate all-graphene circuits [13]. For example, a strip of pure graphene nanoribbon surrounded by fully hydrogenated graphene can serve as transistor channel, while interconnects of these transistors can be made from pristine graphene. The graphane (or other graphene derivatives that has a band

gap) can also be used as active elements, such as optical switch in all-graphene photoelectronics. Moreover, magnetic graphene, such as graphane, would be a ferromagnetic semiconductor used as spin injection sources in all-graphene spintronics.

1.3 Introduction to single walled carbon nanotube

A single-walled carbon nanotube (SWNT) can be viewed as a cylindrically folded graphene nanoribbon [16]. The unit cell of a SWNT can be explained by chiral vector C_h and one-dimensional translation vector T , as illustrated in Figure 1.7. Chiral vector $C_h = na_1 + ma_2$, which connects two equivalent lattice sites O and A on a graphene sheet, defines the circumference of a SWNT. Therefore a pair of integers (n, m) can be used to specify the chiral vector of a SWNT. The translation vector T , which is normal to C_h , is obtained from the intersection with the first lattice point (B) of the honeycomb lattice.

Figure 1.7. Left: Lattice structure of graphene and the unit cell of (4,2) SWNT. Right: a (4, 2) SWNT rolled from graphene nanoribbon. Adapted from Dresselhaus et al. [16].

Since the real-space unit cell of a SWNT is much larger than that of graphene, the one-dimensional Brillouin zone for a SWNT is much smaller than the that of graphene. In reciprocal space, the reciprocal lattice vectors of a SWNT includes K_1 and K_2 as shown in Figure 1.8 (a), where K_1 is in the circumferential direction and K_2 is along the nanotube axis. For a SWNT with infinite length, wave vectors in the direction of K_2 is continuous, while wave vectors in the direction of K_1 is discrete due to quantization of the electron wavevector along the circumferential direction [16]. The N wave vectors K_1 of a SWNT give rise to N cutting lines in the Brillouin zone of graphene, resulting in one-dimensional electronic bands in each line, as illustrated in Figure 1.8 (b).

Figure 1.8. (a) The Brillouin zone of graphene and (4, 2) SWNT. (b) Cutting lines for (4, 2) SWNT in the band structures of graphene. (c) Electronic band structure and (d) density of electronic states of (4, 2) SWNT. Adapted from Dresselhaus et al. [16].

Electronic band structures of a SWNT can be got by superimposing these 1D cutting lines in electronic band structures of graphene [16]. If one of the allowed K_2 wavevectors passes through $K(K')$ point of graphene, the SWNT is metallic, and otherwise it is semiconducting [16]. Figure 1.8 (d) shows the electronics density of states of (4, 2) SWNT. Due to quantization of electronic states in one dimension nature, the electronic band structures of SWNTs possess spike-like DOS, which is known as van Hove singularities (vHSs). The vHSs closer to the Fermi level originate from cutting lines closer to the K point in the Brillouin zone of graphene. The transition of electronic states between the first and second vHSs is of major significance for the optical properties of SWNTs, including absorption and emission of photons. Regarding the electrical transport properties, metallic SWNTs are model systems for studying quantum transport in one dimension, such as ballistic transport, Luttinger liquid, and quantum interference, while semiconducting SWNTs have been employed to fabricate nanotube-based electronics and photonics, such as transistors, photo-detectors and biosensor devices [17, 18].

1.4 Motivation and objectives of the studies

Due to the unique physical and chemical properties of low dimensional carbon materials, carbon nanotubes and graphene-related researches have become hot topics in condensed matter physics and material science in the past two decades [3, 17, 18]. Large scale synthesis and comprehensive characterization of these low dimensional carbon materials are of significant importance for their potential applications, especially for the applications in nanoelectronics, nanophotonics, bio-sensor devices, flexible transparent conductors [1-6, 17, 18]. Doping and decoration have been developed as effective and

useful modification methods for tuning electronic structures of low-dimensional carbon materials [18], which are of great technological importance for control of their properties for particular applications. Hence, with these motivations, the large scale synthesis, modification and characterization of low dimensional carbon materials, including SWNTs, graphene and graphene derivatives, were conducted. There are four objectives in our study, which include (1) wafer-scale synthesis of vertically aligned SWNTs at low temperature (below 500 °C) by plasma-enhanced chemical vapor deposition, which is a crucial step for integration of SWNTs to current Si-based microelectronics; (2) large area and thickness controllable synthesis of graphene layers by low pressure chemical vapor deposition; (3) substitutive doping of graphene with nitrogen and tuning its electronic structures; (4) fabrication of graphene derivatives by surface decoration of graphene and investigation of their electronic structures.

1.5 Organization of this thesis

The structures, electronic structures and applications of three kinds of low dimensional carbon materials, including graphene, graphene derivatives and SWNTs, are introduced in Chapter 1. In Chapter 2, the fabrication methods and Raman spectroscopy of these low dimensional carbon materials are reviewed as the literature background. Chapter 3 presents the plasma-enhanced chemical vapor deposition synthesis and characterization of vertically aligned SWNTs and a new kind of one dimensional carbon materials, linear carbon chain encapsulated inside SWNT ($C_n@SWNT$). Chapter 4 describes the controllable low pressure chemical vapor deposition synthesis and comprehensive characterization of single layer graphene, bilayer graphene, as well as

nitrogen doped single layer graphene. Chapter 5 investigates the hydrogenation of graphene using hydrogen plasma and the evolution of structures and electronic structures of hydrogenated graphene with different amount of hydrogen coverage. Chapter 6 gives the conclusion of this thesis and the perspective of future work.

Chapter 2

Literature Background

2.1 Fabrication of graphene

2.1.1 Micromechanical exfoliation of graphite

It was once believed that free standing graphene, a two dimensional modeling materials established decades ago, does not exist, because the structure of graphene is not stable in theory [1,2]. However, in 2004, K. S. Novoselov *et al.* successfully fabricated graphene for the first time, using a quite simple method, micromechanical exfoliation of graphite by scotch tape [19]. In this method, scotch tape is firstly attached on the surface of graphite, and then graphite thin layers from buck graphite are peeled off iteratively until the contrast of the graphite thin layers on the tape is very weak. Following, the tape with graphite thin layers is adhered to the desired substrate using pressure by hand or tool, and at last the tape is gently removed off. Graphene samples with different layers attached on target substrate by the weak Van de Waals force can be identified by white light contrast on substrates under a microscope, which will be described in details below. By this micromechanical exfoliation technique, graphene with size up to several hundred μm^2 can be easily fabricated. The existence of “structurally unstable” graphene is believed to be attributed to strong C=C bonds in graphene and the unexpected rippled structures, which is revealed by transmission electron microscopy (TEM) investigation of the free standing graphene transferred onto TEM grids [20].

It is interesting that graphene, monolayer carbon atoms, can be seen by naked

eyes under an ordinary optical microscope [19]. The reason is that with the help of an appropriate thickness of SiO₂ on Si substrate, for example 100 nm and 300 nm, the reflected light intensity of graphene get its maximum at around 550 nm, i.e. at the maximum of the human eye sensitivity and the optical contrast of the monolayer carbon on such substrates near this wavelength become sufficient high to make it observable. The origin of the contrast can be explained by Fresnel's equations based on the graphene/SiO₂/Si trilayer system [21].

Taking account of all the wavelength of the white light source equipped in the optical microscope, contrast spectrum generated from a reflection spectrum can be developed to be a quick and quantitative optical method for identification of the number of graphene layers [22]. The contrast spectrum is obtained by the calculation $C(\lambda) = (R_0(\lambda) - R(\lambda))/R_0(\lambda)$, where $R_0(\lambda)$ is the reflectance spectrum from the SiO₂/Si substrate and $R(\lambda)$ is the reflectance spectrum from graphene sheet. For example, Figure 2.1 displays graphene sheet with different number of layers on Si substrate with a 285 nm SiO₂ capping and their corresponding contrast spectra. The observed graphene sheets from one to ten layers show clear contrast difference, but it is hard to distinguish the accurate number of layers by naked eyes. The recorded contrast spectrum for single layer graphene has a peak centered at 550 nm and the contrast peak position is almost unchanged with increasing layers up to 10. The peak value in contrast spectrum for single layer graphene is about 0.09 ± 0.005 , and it increases with the number of layers, for example, 0.175 ± 0.005 , 0.255 ± 0.010 , and 0.330 ± 0.015 for two, three, and four layers, respectively. These significantly different contrast values become accurate indicators for the number of graphene layers [22].

Figure 2.1. The contrast spectra of graphene sheets with different thicknesses, together with the optical image of all the samples. Adapted from Ni et al. [22].

2.1.2 Chemical vapor deposition of graphene

Although fabrication of graphene with size of 1 mm^2 by micromechanical exfoliation technique has been achieved in some research groups, micromechanical exfoliation of graphite is still not a mature method for future commercial application of graphene [3]. Other methods, such as epitaxial growth of graphene on SiC crystals and chemical vapor deposition (CVD) of graphene on metallic substrates, have been studied for a few years [3,23]. The epitaxial growth of graphene on SiC substrates is performed

by heating SiC to high temperature (~ 1200 °C). For this method, there are some drawbacks, including graphene buffer layer covalently bonded to SiC substrates, high cost of single crystalline SiC substrates, limited SiC wafer size, and ultrahigh vacuum conditions. While synthesis of graphene by CVD method shows promising potential for technological applications of graphene [24]. In 2009, a significant progress, growth of pure single layer graphene on copper (Cu) foils in large scale, was reported by Li *et al.* [25]. They grew graphene by pyrolysis of methane and hydrogen on Cu surface at temperature up to 1000 °C. Because of poor solubility of carbon atoms in Cu, more than 95% single layer graphene coverage on Cu surface can be obtained. As shown in Figure 2.2, the as-synthesized graphene films on Cu foils can be further transferred onto arbitrary substrates in large area by a wet chemical etching and transfer process [24, 25].

With carbon isotope (C_{13}) labelling technique, it was demonstrated that graphene growth on polycrystalline Cu surface was a surface-catalyzed and self-limiting process [26]. The as-grown graphene are polycrystalline with domains having an area of tens of square micrometers. The growth kinetics study revealed that the domain size of graphene could be enlarged by adjusting the growth parameters such as temperature (T), and methane flow rate (J_{Me}) and partial pressure (P_{Me}). As shown in Figure 2.3, the density of graphene nuclei can be decreased (domain size increases) as T is increased, or as J_{Me} and P_{Me} are decreased, respectively. Therefore high T and low J_{Me} and P_{Me} yield a low density of graphene nuclei and large domain size [27]. With optimized growth parameters, graphene films with domains having an area of hundreds of square micrometers can be obtained. Electrical transport measurements performed on such graphene films exhibited high carrier mobility up to about $16,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature [28].

Figure 2.2 (a) SEM image of graphene transferred on 285 nm SiO_2/Si showing wrinkles, (b) optical microscope image of the same regions as (a). (c) and (d) Graphene films transferred onto SiO_2/Si and glass substrates, respectively. Adapted from Li et al. [25].

Figure 2.3 SEM images showing the evolution of the size of graphene grains grown under different growth conditions. Adapted from Li et al. [27].

2.2 Hydrogenation of graphene

K. S. Novoselov *et al.* demonstrated the first effort to fabricate graphane through hydrogenation of free-standing graphene membranes fixed to micro metal scaffolds, which are two sides available for attachment of H atoms [11]. The H atoms were produced by remote hydrogen plasma and the samples were placed 30 cm away from the plasma zone. Such hydrogenation approach typically required 2 hours of plasma treatment to reach the saturation of hydrogenation on graphene [11]. TEM investigation revealed that the hydrogenation on the free-standing graphene is ununiform and the hydrogenated domains preserved the hexagonal lattice with a much shorter lattice constant than that of graphene, indicating the formation of a graphane structure in these regions. The fact that there are small fractions of graphane domains embedded in graphene is consistent with Raman spectrum shown in Figure 2.5. Since graphane is an insulator with a large (~ 3.5 eV) band gap, Raman signal of single layer graphane probed by visible laser should be extremely weak and Raman spectrum of graphane should be significantly different from that of graphene. Therefore the Raman spectrum of hydrogenated free-standing graphene displayed in Figure 2.5 is mainly attributed to unhydrogenated graphene and the graphane domains contribute as defects.

Single side hydrogenation of graphene on SiO_2/Si substrates was also studied in their experiment, which transformed the highly conductive semimetal into a localized insulator [11]. The hydrogenation is found to be reversible after thermal annealing. The original metallic state and even the quantum Hall effect can be restored by annealing [11]. Under the same hydrogenation conditions, bilayer graphene samples show a substantially lower level of hydrogenation than single layer graphene [11]. It is believed that the

atomic hydrogenation is facilitated by the rippled convex surface on graphene surface, where the lattice is already deformed in the direction that favors sp^3 bonding. This picture is in agreement with the fact that bilayer graphene is less rippled than single layer graphene and explains the ununiform hydrogenation mentioned above [20].

Figure 2.5. Changes in Raman spectra of graphene caused by atomic hydrogenation. (a) Single side hydrogenation of Graphene on SiO_2/Si . (b) Double side hydrogenation of free-standing graphene. Red, blue, and green curves correspond to pristine, hydrogenated, and annealed samples, respectively. (Left inset) Raman spectra of hydrogenated graphene on SiO_2 (blue curve) and graphene membrane (black curve), which are in a partially hydrogenated state achieved after 1 hour of simultaneous exposure of atomic hydrogen. (Right inset) TEM image of graphene membrane that partially covers the aperture 50 μm in diameter. Adapted from Novoselov et al. [11].

Scanning tunnelling microscopy (STM) was performed to study the adsorbate structures of hydrogen atoms on the basal plane of epitaxial graphene grown on a SiC substrate [29]. Atomic hydrogen generated from a hot (1600 K) hydrogen atom beam source was used to hydrogenate the graphene on single side. The convex areas were viewed as precursors for carbon puckering, and therefore energetically favourable binding sites for hydrogen atoms. At low coverage the formation of hydrogen dimers occurs preferentially on the convex areas. As illustrated in the left of Figure 2.6, the coadsorbed pairs of H atoms are mainly in the forms of either neighboring C atoms (1,2-dihydrogenated ring, ortho-dimer) or opposite C atoms (1,4-dihydrogenated ring, para-dimer), which are the most energetically stable configuration predicted by DFT calculation. With increasing coverage, hydrogen atoms tend to form larger hydrogen clusters in a disordered manner, as shown in the right of Figure 2.6.

Figure 2.6. Left: STM image of hydrogenated graphene. The inset shows the schematic of the (A) ortho- and (B) para-dimer configuration on the graphene lattice. Right: STM image of the graphene surface with high hydrogen coverage. The bright protrusions in the image are identified as atomic hydrogen clusters. Adapted from Balog et al. [29].

2.3 Synthesis of vertically aligned single walled carbon nanotubes

2.3.1 Thermal chemical vapor deposition

The unique physical and chemical properties of SWNTs provide promising potential for a wide range of technological applications. Initial synthesis of SWNTs was carried out using electric arc discharge and laser ablation techniques, which can produce high synthesis temperatures (~3000-4000 °C) for vaporization of solid carbon sources [17, 18]. However the available quantity is limited for these synthesis methods. Thermal CVD had later been developed to be a successful method for large-scale synthesis of SWNTs [17, 18]. In this method, the hydrocarbon compound vapor decomposes at relative lower temperatures (~700-1000 °C) and forms SWNTs in the presence of the metal catalyst with very small sizes (1~2 nm) [17, 18]. Generally, the metal catalysts are cobalt (Co), nickel (Ni) and iron (Fe) nanoparticles synthesized by chemical solution methods or physical vapor deposition methods.

Well-defined arrangements and configurations of SWNTs, including horizontal and vertical alignment on a substrate, are particularly important to enable both fundamental studies and potential applications, such as nanoelectronics, sensor devices, field emission devices and interconnects [18]. The first successful synthesis of vertically aligned SWNTs (VA-SWNTs) on a flat substrate was demonstrated by alcohol catalytic thermal CVD in 2004, where low pressure pyrolysis of ethanol vapor at 800 °C was employed for growth SWNT films on densely mono-dispersed Co-Mo catalyst of 1-2 nm size [30]. One of the breakthroughs since then is the growth of millimeter long VA-SWNTs using water assisted ethylene CVD at atmosphere pressure [31]. The SWNTs are well aligned in the forest due to van der Waals force. The proper amount of water (100

ppm) act as etching agents to remove the carbon coating deposited on catalysts and extend catalyst lifetime. Moreover, a thin Fe catalyst layer (about 0.5~1 nm) and alumina (10 nm Al_2O_3) catalyst buffer layers employed in their growth process had been demonstrated to be important factors for significantly enhanced catalyst activity [31]. A few years later, without any oxygen containing gas sources as etching agents, Kayastha *et al.* had synthesized VA-SWNTs by controlling the supply of acetylene source gas and the thickness of Mo/Fe/Al (0.1 nm/0.5 nm/10 nm) trilayer catalyst films [32]. Figure 2.8 shows scanning electron microscopy (SEM) images, high resolution transmission electron microscopy (HRTEM) images and the corresponding Raman spectra of their as-synthesized SWNT films.

Figure 2.8. SEM/HRTEM images and Raman spectrum of the VA-SWNT film (laser excitation wavelength is 633 nm). Adapted from kayastha *et al.* [32].

2.3.2 Plasma-enhanced chemical vapor deposition

Plasma enhanced CVD (PECVD), in comparison to conventional thermal CVD, is well known to have advantage of lowering the synthesis temperature via plasma-assisted dissociation of the carbon feedstock molecules and activating catalysts via plasma-heating [33,34]. Thus the low temperature synthesis of VA-SWNTs using PECVD method is highly desirable and currently is an active research topic, especially for some applications based on current integrated circuit technology, such as vacuum electronics and interconnects. However, early attempts to use PECVD process to synthesize carbon nanotube yielded mostly multi-walled nanotubes and nanofibers [33,34]. Goheir *et al.* showed that the exposure of metal catalyst to the plasma sheath of distributed electron cyclotron resonance (DECR) plasma inevitably resulted in the transition of SWNTs to MWNTs, which was attributed to ion bombardment effects in high density plasma created by DECR source [35]. In their plasma sheath, there was a high density of plasma ion flux ($n_{\text{ion}} \sim 10^{10}/\text{cm}^3$) which bombarded SWNTs at sufficiently high energy of ~ 100 eV and caused C-C bond breakage. The excessive plasma etchings damage SWNTs and favor the synthesis of multi-walled nanotubes which are more resistant to plasma etchings. In order to synthesize SWNTs, it requires the use of special plasma configuration to minimize the explosion of catalyst and as-grown SWNT to the plasma sheath.

With a home-built radio frequency (13.56 MHz) remote PECVD, Li *et al.* synthesized large-scale VA-SWNTs on 0.2 nm Fe/SiO₂/Si catalyst substrates at 720°C [36, 37]. Their system was shown in Figure 2.9 (a), in which the plasma discharge was operated at low plasma power (60 W) in capacitively coupled mode. The created low-density plasma can diffuse down to catalyst substrates placed 40 cm away from the

plasma coil and therefore a discharge sheath close to the substrate was avoided, which resulted in significant reduction of ion bombardments [36]. Similarly, Zhong *et al.* demonstrated synthesis of VA-SWNTs with a remote point-arc microwave PECVD system, which was displayed in Figure 2.9 (b) [38]. The high-density microwave plasma ball was generated at a point electrode located far above the catalyst substrates. Due to eliminated plasma ion bombardment etching effect, sub-millimeter long VA-SWNTs was successfully synthesized on Al/Fe/Al (0.5 nm/0.5 nm/10 nm) trilayer catalyst films at relatively low temperature, 600 °C [38].

Figure 2.9. Schematic diagrams of (a) radio frequency remote PECVD system and (b) point-arc microwave PECVD system. Adapted from Li *et al.* [36] and Zhong *et al.* [38].

The presence of plasma radicals such as H plays another important role, selective etching effect on the as-grown SWNTs [36, 37]. Zhang et al showed that methane plasma selectively etched metallic SWNTs while semiconducting SWNTs remained unmodified [39]. Metallic SWNTs were irreversibly etched into hydrocarbon gas species as a result of ion bombardment of H and CH₃ ion species present in methane plasma. Small-diameter SWNTs were preferentially etched over larger ones because of the higher radius curvature and strain in the C-C bonding [39]. This finding had great implication for controlling the electronic properties of SWNTs synthesized by PECVD. Theoretical studies had predicted that ~1/3 of as-synthesized SWNTs was metallic and the remaining ~2/3 nanotubes were semiconducting [17]. On the contrary, preferential synthesis of semiconducting SWNTs can be achieved in a PECVD process, whereby the metallic SWNTs will inherently destroyed during the synthesis steps [36, 37].

2.4 Raman spectroscopy of low dimensional carbon materials

2.4.1 Raman spectroscopy of graphene

Raman spectroscopy has been playing an important role in the study of low dimensional carbon materials, including graphene and SWNTs [16, 40]. Due to their special electronic band structures, incident photon or scattering photon can match the electron transition in real electronic states, resulting in resonance behavior for probing laser excitations. Therefore, both the structural and electronic characteristics can be extracted from Raman spectrum. The strong resonance effect also causes extremely strong Raman signal, which make Raman spectroscopy study of individual SWNT and single layer graphene possible. The fundamental aspects for the Raman spectroscopy

study of graphene and SWNTs can be found in some comprehensive reviews [16, 40].

There are two characteristic Raman features of graphene, including the so called G band located around 1580 cm^{-1} and 2D (G') band located around 2680 cm^{-1} , which are shown in Figure 2.10. For defective graphene, there are also defect induced D band located around 1350 cm^{-1} and D' band located around 1620 cm^{-1} . The G band originates from single resonance process associated with doubly degenerate iTO and LO phonon mode (in-plane vibration between the two dissimilar carbon atoms A and B in the unit cell) at the Brillouin zone center (Γ point) [40]. As illustrated in Figure 2.11, electron with wave vector k (measured from K point) absorbs the incident photon energy and is excited to the conduction band. Subsequently, the electron encounters an inelastic scatter by the iTO or iLO phonon at Γ point. Following is the emission of a photon due to recombination of electron and hole.

Figure 2.10. Raman spectrum of a graphene edge measured with 2.41 eV laser energy.

Adapted from Malard et al. [40].

Figure 2.11. Illustration of Raman scattering process for the D, D', G and G' (2D) bands of graphene. Adapted from Malard et al. [40].

As schematically shown in Figure 2.11, the D and 2D (G') bands originate from a double resonance Raman process involving iTO phonon along the KM direction as well as inter-valley scattering of photo-excited electrons along the $K\Gamma$ direction [40]. While the D' band originates from a double resonance Raman process involving iLO phonon near Γ point and intra-valley scattering of photo-excited electrons [40]. For double resonance process of 2D band, electron with wave vector k (measured from K point) is excited to conduction band by incident photon, following inelastic scattered by a iTO phonon (phonon with momentum q) to a circle round K' point. After that, the electron is inelastically scattered back by an iTO phonon with reverse momentum direction $-q$, followed by the recombination of electron and hole. Triple resonance Raman process is also possible for 2D band, where scattering of electron from the K (K') point to K' (K) point and simultaneous scattering of the hole from the K (K') point to K' (K) point. According to the double-resonance nature of 2D and D bands, different excitation

energies excite electrons with different wave vector k , resulting in different frequencies of phonon involved in inelastic scatterings, and therefore the excitation energy dependence of D and 2D bands can be used to explore the electronic band structures of graphene around K and K' point [40].

Figure 2.12. Left: 2D Raman bands measured with 2.41 eV laser energy for (a) 1LG, (b) 2LG, (c) 3LG, (d) 4LG, (e) HOPG. Right: Schematic view of double resonance Raman processes based on split electronic bands of bilayer graphene (2LG). Four double resonance Raman processes are indicated: (a) process P11, (b) process P22, (c) process P12, and (d) process P21. Adapted from Malard et al. [40].

The 2D band of SLG is a single, sharp and symmetric peak with a full width at half maximum (FWHM) of $\sim 30 \text{ cm}^{-1}$. Actually, the shape, width, and position of 2D band of graphene show significant dependence on graphene layer number [40]. The evolution of the 2D band as a function of the number of layers for 514.5 nm (2.41 eV) excitation was demonstrated in the left of Figure 2.12. The 2D band becomes broader and blue-shifted when the graphene layer number increases from single layer graphene to multilayer graphene [40]. As the 2D band originates from a two phonon double resonance process, it is closely related to the band structures of graphene layers. Ferrari et al. have successfully explained the broadening of the 2D band based on the splitting of electronic band structures in multilayer graphene [41]. Figure 2.12 (right) shows a detailed description of the origination of four components in 2D band observed for AB stacked bi-layer graphene. The strong interaction of the graphene planes in AB stacked bi-layer graphene causes the π and π^* bands to split into four bands. Due to optical selection rules, the incident photon can couple only two pairs of the four bands, as illustrated in the right of Figure 2.12. The inelastically scattered electrons can be adopted by both the upper and lower electron bands, resulting in four processes involving iTO phonons with different momenta around K . Due to strong phonon dispersion along the KM direction, four phonon momenta corresponds to four distinguishing phonon frequencies, and therefore four components in 2D Raman band for bilayer graphene [40].

2.4.2 Raman spectroscopy of single walled carbon nanotube

In comparison to Raman spectrum of graphene, Raman spectrum of SWNT demonstrates additional characteristic Raman modes, including radial-breathing mode

(RBM) located at low frequencies ($100\sim 400\text{ cm}^{-1}$), split G bands, enhanced M and iTOLA bands [16], as shown in Figure 2.13. The origination of RBM Raman modes is coherent vibration of the C atoms in radial direction, which is illustrated in Figure 2.14 (a). The RBM can be used to study the nanotube diameter (d_t) through the relation $\omega_{\text{RBM}} = A/d_t + B$, a quite general relationship derived from the continuum mechanics of a small hollow cylinder. The A and B parameters can be determined experimentally. For typical SWNT bundles in the diameter range $d_t = 1.5\pm 0.2\text{ nm}$, $A = 234\text{ cm}^{-1}\text{ nm}$ and $B = 10\text{ cm}^{-1}$ have been found, where B is an up-shift in RBM due to tube-tube interaction [16].

As shown in Figure 2.13, the split G bands of metallic and semiconducting SWNTs have significant differences in peak shapes, which can be used to distinguish between metallic and semiconducting SWNTs [16]. The origination of split G band feature for semiconducting SWNTs is the phonon wave vector confinement along the SWNT circumferential direction. The G+ peak located around 1590 cm^{-1} is associated with carbon atom vibrations along the nanotube axis, while the G- peak located around 1570 cm^{-1} is associated with vibrations of carbon atoms along the circumferential direction of the SWNT, as illustrated in Figure 2.14 (b). The G+ frequency keeps nearly constant for SWNT with different diameter, however, the curvature-induced softening of G- frequency shows strong dependence on the diameter of SWNT [16]. In contrast, the G+ peak ($\sim 1590\text{ cm}^{-1}$) of metallic SWNT has been assigned to TO phonons along the circumferential direction, and the G- peak ($\sim 1550\text{ cm}^{-1}$) is associated with LO phonons along the nanotube axis [42]. The origination of split G band feature for metallic SWNT is Kohn anomaly effect, which strongly reduces the frequency of the axial LO phonons [42]. Due to one-dimensional nature of SWNT, the Kohn anomaly caused by electron-

phonon coupling in metallic SWNT is larger than those in graphene and graphite. Apparently, the softening of G- band by the electron-phonon coupling is much larger than the curvature-induced softening of G+ band.

Figure 2.13. (a) Raman spectra from a metallic and a semiconducting SWNT. (b) The G band for highly oriented pyrolytic graphite (HOPG), a semiconducting SWNT and a metallic SWNT. Adapted from Dresselhaus et al. [16].

Figure 2.14. Schematic picture showing the atomic vibrations for (a) RBM and (b) G band modes of a semiconducting SWNT. Adapted from Jorio et al. [43].

The M band near 1750 cm^{-1} is related to the out-of-plane (oTO) mode near Γ point, an infrared-active mode at 867 cm^{-1} . It is not a Raman-active mode, but its overtone appears in Raman spectrum through double resonance Raman process [16]. The so-called iTOLA band ($\sim 1950\text{ cm}^{-1}$) is attributed to a combination mode of the in-plane transverse optical mode (iTO) near Γ point and the longitudinal acoustic (LA) mode near Γ point, iTO+LA. Similarly, iTOLA band is activated by double resonance Raman process [16]. The M band and iTOLA band can also be observed in Raman spectra of few layer graphene and graphite. However, it is believed that they are enhanced in the Raman spectrum of SWNT due to van Hove singularity effect and symmetry-breaking effect [16].

Chapter 3

Low Temperature Synthesis of Single-walled Carbon Nanotubes (SWNTs) and C_n@SWNTs

3.1 Introduction

The choice of synthesis technique is highly motivated by the field of applications. For application of carbon nanotubes (CNTs) in microelectronics, such as interconnects and vacuum electronics, low temperature synthesis of CNTs is a crucial step to incorporate CNTs into the integrated circuit, since in present back-end CMOS technology the wafers can only resist the temperatures lower than 500 °C for a limited time without major degradation of electronic performance. Capacitively coupled radio-frequency (CC-RF) PECVD has been traditionally used in low temperature manufacturing of integrated circuit and therefore existing facilities are suitable for large-scale and commercially viable synthesis of CNTs [44]. Without using of special plasma configuration such as remote plasma, we explored low temperature and large-scale synthesis of VA-SWNTs on substrates directly exposed to the discharge sheath in a CC-RF PECVD system, which has a capacity for loading 8 inch Si wafers.

Linear *sp*-hybridized carbon chains are considered as fundamental constituents of the interstellar medium and have significant scientific interests due to its really one dimensional nature [45]. The infinite chain of *sp*-hybridized carbon is known as carbyne, another allotrope of carbon [46]. The structure of carbyne is theoretically predicted as a polyyne-like structure with alternating single and triple bonds [46]. In comparison to

intensive study of synthesis techniques for sp^2 -hybridized carbon, the synthesis technology for sp -hybridized carbon is not well developed. There are only a few reports on synthesis of sp -hybridized carbon chain by gas-phase deposition techniques and organic chemical synthesis [45, 46]. For example, sp -hybridized carbon chain with contiguous long acetylenic carbons can be synthesized by means of condensation polymerization [46]. In our low density plasma system, linear sp carbon chains was found to be encapsulated within SWNTs when a special catalyst was employed, forming a C_n @SWNTs hybrid system. Raman spectroscopy and electron microscopy were employed for insensitive characterization of the sp -hybridized carbon chains. The electron transport properties of C_n @SWNT bundles were measured at varying temperature, which indicated the C_n @SWNT was a new type of one dimensional quantum conductors.

3.2 Synthesis of vertically aligned SWNTs by plasma-enhanced chemical vapor deposition

3.2.1 Experimental

Figure 3.1 (a) shows the CC-RF PECVD system used for synthesis of VA-SWNTs. A schematic diagram of this system is displayed in Figure 3.1 (b). RF (13.56 MHz) source is coupled to the plasma via a parallel-plate capacitor, in which RF power source was connected to the upper stainless steel electrode (cathode) and the grounded 8 inch molybdenum (Mo) plate works as heating stage and bottom electrode (anode). The plasma was generated between the two electrodes with 4 cm separation. Figure 3.1 (c) showed a typical glow discharge encountered in our PECVD reactor. The plasma is

composed of electrons, charged ions, neutral radicals and neutral molecules, and there is a spontaneous but non-equilibrium conversion of neutral species into long-lived radicals for CVD. The electron density in the CC-RF plasma is $\sim 10^8$ - 10^9 cm^{-3} , which is much lower than those in high-density plasma generated by inductively coupled RF discharge and electron cyclotron resonance microwave discharge [44]. In addition to the bright plasma region in discharge, there are two discharge sheaths, dark regions in discharge, near the upper and bottom electrodes. Sheath voltages were formed across these dark regions with the electrodes and the plasma region [44]. The ions in discharge sheath were accelerated by the sheath voltages and the anode sheath voltages equals the plasma potential (V_p , in tens of voltage) [44]. The catalyst substrate is placed in anode sheath, where the ion bombardment is much weaker than that in cathode sheath [44].

Figure 3.1 (a) A radio-frequency PECVD system, (b) a schematic diagram of the main components of PECVD system, (c) plasma ignited in PECVD system.

For growth of VA-SWNTs, 1 nm-thick iron layer was used as the catalyst, deposited on native oxide covered Si substrates by electron beam evaporation. The PECVD reactor was evacuated to a base pressure (< 0.5 Pa), and then admitted to 40 sccm flowing hydrogen (H_2), with 1 Torr (133 Pa) gas pressure being maintained. The Mo stage was heated by a graphite heater to a temperature in the range of 500-600 °C in 10 min. The substrate temperature was maintained constant, as measured by a K-type thermocouple placed near the substrate above the Mo stage. After the H_2 plasma was ignited at the growth temperature, ethylene (C_2H_4) was introduced for 5 min to grow carbon nanotubes and the pressure was adjusted to a desired value. The H_2/C_2H_4 flow rate was maintained at 40 sccm/10 sccm (sccm denotes cubic centimeter per minute) during the process. To study the ion bombardment effect, the gas pressure of the PECVD chamber could vary in the range of 0.2-10 Torr, and the plasma input power might change between 5W and 100W in various experiments. The plasma-heating effect could be ignored in these studies as the plasma was operated at low power densities and moderate gas pressures. The as-grown VA-SWNTs samples were characterized by SEM (JEOL 6700), Raman spectroscopy (Renishaw inVia Raman spectrometer) with laser excitation of 785 nm (1.58 eV), and high resolution transmission electron microscopy (HRTEM, JEOL 2010F operating at 200 kV).

3.2.2 Low temperature synthesis of vertically aligned SWNTs

The catalyst, 1 nm-thick Fe layer on a Si substrate, was reduced by H_2 during heating up to 500 °C in 10 mins. The growth was then performed at 500 °C, 3 Torr pressure, and 40 sccm H_2 /10 sccm C_2H_4 . The plasma input power was changed from 30

W, 15 W, to 7 W respectively. Ultrathin Fe films as the catalyst for SWNT growth were reported in literature [37]. Atomic force microscopy (AFM) studies showed that they were not continuous films, but composed of nanoscaled islands [47], which should be essential for the SWNT nucleation. The SEM images in Figure 3.2 show that our CNTs, grown at 500 °C, 3 Torr and 7-30 W, are dense and vertically aligned. The maximal length of the CNTs is about 4 μm while the length of the CNTs in Figure 3.2 (c) (with 7 W input power) is obviously shorter. The Raman spectra of the VA-CNT samples are shown in Figure 3.3. The Raman spectrum in Figure 3.3 with 30 W input power is typical of MWNTs, with a very strong D band at $\sim 1300\text{ cm}^{-1}$, which is associated with defects in CNTs [16].

Figure 3.2 SEM images of VA-CNTs synthesized at 500 °C with 3 Torr pressure and different input power. (a) 30 W, (b) 15 W, (c) 7 W.

When the plasma input power is decreased to 15 W, the intensity of D band decreases relatively with respect to G band at $\sim 1595\text{ cm}^{-1}$. A very weak RBM and small intensity double resonance features labeled as M and iTOLA bands appear at ~ 215 , 1768 and 1860 cm^{-1} respectively. As introduced in chapter 2, M band is the overtone of oTO, the out-of-plane mode at 867 cm^{-1} , while iTOLA refers to second order combination mode of in-plane tangential optical phonon mode (iTOL) and longitudinal acoustic mode (LA).

These bands are characteristic of SWNTs [16]. The observation of these features is therefore indicative of the existence of SWNTs in the samples. Further reducing the plasma input power to 7 W results in very clear RBM bands as well as the greatly-reduced I_D/I_G ratio, confirming the existence of abundant SWNTs due to the low plasma input power. The diameter of the SWNTs ranges between 1 to 1.3 nm, according to the formula $w_{\text{RBM}} = 234/d_{\text{SWNT}} + 10$ [16]. Moreover, G band is observed to split into G⁻ band and G⁺ band. The sharp Lorentzian features of the peaks indicate that the SWNTs probed by the 785 nm laser excitation were mainly semiconducting [16]. It can be concluded that the VA-SWNTs could be synthesized by CC-RF PECVD at a relatively low temperature (500 °C), if the plasma input power was sufficiently low, regardless of the catalysts being directly exposed to the discharge sheath.

Figure 3.3 (a-c) Raman spectra of VA-CNTs shown in Figure 3.2, and (d) VA-SWNTs synthesized with Cu mesh cover for protection. The configuration of the Cu mesh cover is illustrated in the inset.

The HRTEM images in Figure 3.4 demonstrate that most of the CNTs grown at 500 °C, 3 Torr and 15 W are few-walled (3-6 walled) with the diameter of about 5~7 nm. Figure 3.4 (c) and (d) show a SWNT bundle and an isolated SWNT respectively, in the sample with 7 W plasma input power. The wall of the isolated SWNT is not smooth, but indented as shown by the arrows in Figure 3.4 (d). Both the substantive structure defects of the SWNTs synthesized with 7 W input power and the structure transformation to few-walled CNTs synthesized with increased input power should be attributed to the ion bombardment etching effect. During the growth of CNT in discharge sheath, C-C bonds breaking caused by ion bombardment compete with the formation of catalyzed carbon nanotubes [35]. If the growth-rate was low, SWNT growth by PECVD was observed to involve a transition from SWNTs to MWNTs [35]. In the case of low rate growth high plasma power might etch SWNTs away totally due to increased ion bombardments. However, MWNTs with higher resistibility against ion etching could grow on the same catalyst after the SWNTs were etched away [35]. Our studies at 500 °C were a low-rate growth process. With reducing the ion etching via lowering the plasma input power, SWNTs dominate in the sample grown at 7 W, few-walled CNTs at 15 W, while MWNTs at 30 W respectively.

The above explanation can be verified by a special experiment. Noticeably, under a growth condition typical for MWNTs, i.e. 500 °C, 3 Torr and 30 W, SWNTs could be successfully grown by placing a copper (Cu) mesh 2 mm above the catalyst substrate to shield the ion bombardments (see the inset of Figure 3.3). The Raman spectrum of the as-grown SWNTs shown in Figure 3.3 (d) is characteristic of SWNTs with rather low D band, indicating the high quality of the SWNTs sample with limited ion bombardments.

The above results indicate that at a relatively low temperature (500 °C), the alleviation or elimination of ion bombardments plays a crucial role for VA-SWNTs growth. By reducing the plasma input power or with special configuration the high-quality growth of VA-SWNTs is achievable.

Figure 3.4 HRTEM images of CNTs synthesized at 500 °C with 3 Torr pressure and different plasma power. (a, b) 15 W, (c, d) 7 W.

3.2.3 Ion bombardment effect

In order to investigate the influence of growth parameters such as temperature, plasma power and pressure on the ion bombardment effect, the growth temperature was elevated to 600 °C. Figure 3.5 shows the Raman spectra of VA-CNTs synthesized at 600 °C with 3 Torr pressure and input RF power of 7 W, 15 W, 30 W, 50 W and 100 W respectively. All the Raman spectra reveal RBM signals characteristic of SWNTs. At 7 W and 15 W, strong RBM signal, low I_D/I_G ratio (0.06-0.12), and well-resolved G splitting (G- band and the G+ band) indicate the high quality of VA-SWNTs. With increasing the plasma power, the defects related D-band intensity increases gradually, most probably due to enhanced ion bombardments. However even at 100 W, RBM peaks and Lorentzian feature of G band are still observable, which means that there still exists certain amount

of SWNTs in the as-grown products.

Figure 3.5 Raman spectra of VA-CNT samples synthesized at 600 °C with 3 Torr pressure and different input power. (a) 15 W, (b) 30 W, (c) 50 W, (d) 100 W.

Figure 3.6 Raman spectra of VA-CNT samples synthesized at 600 °C with input power of 50W and different pressure. (a) 0.2 Torr, (b) 1 Torr, (c) 3 Torr, (d) 6 Torr, (e) 10 Torr.

In comparison with the Raman spectra in Figure 3.3, the above results indicate that the operation range of plasma input power for synthesis of VA-SWNTs directly in sheath at 600 °C is broader than that at 500 °C, i.e. the resistibility against ion bombardment etching of the SWNTs synthesized at 600 °C is much higher than that of 500 °C. This can be well interpreted by the above-mentioned two competitive processes, i.e. catalytic growth of C-C bonds on nanoparticle catalysts and C-C bonds breaking caused by ion bombardment etching. At 600 °C the growth rate and tube quality of SWNTs are higher than that of 500 °C under the same plasma conditions, and hence SWNTs synthesized at 600 °C are less susceptible to ion bombardment etching. It should be noted that with 7 W and 15 W plasma input power RBM signal is peaked at high wave numbers corresponding smaller diameters (1-1.1 nm), while with 30 W and 50 W the RBM signals with small diameters decrease significantly. This may indicate that small-diameters SWNTs could be easily etched away at elevated plasma powers, due to higher curvature and higher strain of the carbon network [39].

The influence of pressure on the ion bombardment effect was investigated by fixing temperature at 600 °C, plasma input power at 50 W, and varying gas pressures from 0.2, 1, 3, 6 to 10 Torr. It is noted that CNT growth by CC-RF PECVD is normally operated in the collisional sheath at moderate-pressures (≥ 1 Torr) [44]. With low pressure (0.2 Torr), the growth may take place in the collisionless region [44]. Raman spectrum in Figure 3.6 reveals that the CNTs grown at 600 °C, 50 W and 1 Torr are SWNTs with characteristic RBM peaks, low I_D/I_G ratio (0.16) and clearly splitted G^+ and G^- . The SEM image in the inset of Figure 3.7 (a) shows that the length of SWNTs in this sample are about 4 μm long, with high density and good alignment. The HRTEM image

in Figure 3.7 (b) also confirms that the sample is composed of SWNTs bundles with SWNT diameters of 1-2 nm.

Figure 3.7 VA-SWNTs synthesized at 600 °C with input power of 50 W and pressure of 1 Torr. (a) A slanted view SEM image under low magnification. The inset is a magnified image showing the alignments of the SWNTs. (b) HRTEM image of SWNT bundles.

At low gas pressure 0.2 Torr, the growth of VA-SWNTs was still successful as evidenced by strong RBM peaks. But the length of the VS-SWNTs grown at 0.2 Torr pressure was much shorter (< 600 nm), which should be attributed to low growth rate due to low ionization rate of capacitively coupled RF discharge (10^{-6} - 10^{-3}) [44, 48]. The high I_D/I_G ratio (0.55) in Fig. 5a indicates that there exist substantial amount of defects in the sample grown at 0.2 Torr. This could be due to violent ion bombardments in collisionless sheath of low pressure plasma [44, 48]. With increasing gas pressure to 3-10 Torr, the I_D/I_G ratio dramatically increases to 0.4-0.7, while separation of G- and G+ bands is observable but not well resolved. These indicate that the as-synthesized VA-CNTs are

mostly few-walled carbon nanotubes. It is obvious that the gas pressure could affect the PECVD growth and the structure of VA-SWNTs, and there is an optimal pressure (1 Torr in this example), lower or higher gas pressures than which would result in stronger ion bombardments.

The etching effects of the ion bombardment are dependent on two key parameters, i.e. ion bombardment energy (E_i) and ion flux (J_i). For capacitively coupled RF PECVD operated at moderate pressures (≥ 1 Torr) the plasma sheath is highly collisional [44, 48], and based on a simplified ion space-charge-limited model [49], we can obtain

$$E_i \propto V^{4/5} p^{-1/2} \quad (3.1)$$

$$J_i \propto V p^{3/4} \quad (3.2)$$

where p is gas pressure in Torr, and V the sheath voltage. As the native oxide on doped Si wafer is very thin, the charging effect can be ignored, and therefore the anode sheath voltage V should equal the average positive plasma potential V_p [44]. As described in [48, 49], at a fixed moderate pressure, the plasma potential V_p varies in a very small range if the input power varies in moderate range, while the ion flux increase with increased input power. Therefore, the enhanced ion bombardment etching effect with increased input power should not be attributed to the elevated ion bombardment energy but the increased ion flux. With a fixed input power, when the input power is in the moderated range, $V_p \propto p^{1/2}$ the pressure dependence of ion-bombardment energy and the ion current density are in the forms of $E_i \propto p^{-1/10}$ and $J_i \propto p^{5/4}$, which indicate that the ion-bombardment energy is also weakly dependent on pressure, while the ion flux increases rapidly with increased pressure. Again, we can get the conclusion that the enhanced ion bombardment damage with increased pressure is due to the increased ion flux, while the ion-bombardment

energy is almost constant with increased pressure.

Through the above analysis, we get the useful information that the ion bombardment energy varies in very small range in our PECVD process and the crucial factor for ion-bombardment etching effect is mainly the ion flux. The enhanced ion bombardment etching effect on the synthesized SWNTs with increased input power and pressure is attributed to the increased ion flux. For synthesis of high quality SWNTs directly in sheath, the ion flux should be kept at a sufficiently low level. As the concentration of carbonaceous radicals is about tenfold the ion and electron density [44], sufficient ion and electron density is need to supply enough carbonaceous radicals for SWNT growth. Therefore, the input power and pressure of the PECVD process should be kept an optimal level. In fact, the capacitively coupled radio frequency discharge belongs to low-density plasma, and its ion density is intrinsically low [44]. This may be one of the explanations why high quality VA-SWNTs can be directly synthesized in sheath of capacitively coupled radio frequency discharge with proper input power and pressure, while it is hard to synthesize VA-SWNTs directly in sheath of high-density plasma configurations, such as inductively coupled RF discharge and electron cyclotron resonance microwave discharge [35].

3.2.4 Selective etching effect

The selective etching effect, another important effect in PECVD synthesis of SWNTs, was firstly revealed in PECVD synthesis of SWNTs using a remote plasma and further developed for selective etching of metallic SWNTs in 2006 in Dai's group [36,39]. We also observed that the small-diameter SWNTs could be etched away at elevated

plasma powers in last section. This effect in our PECVD process was further investigated by Raman spectroscopy study of the VA-SWNTs samples synthesized with different H₂/C₂H₄ ratio. The VA-SWNTs were grown at fixed temperature at 600 °C, plasma input power at 15 W, gas pressure at 3 Torr and varying H₂/C₂H₄ ratio as 20 sccm/40 sccm, 30 sccm/30 sccm, 40 sccm/10 sccm, and 40 sccm/5 sccm. When the H₂/C₂H₄ ratio is not smaller than 1, the as grown CNTs are SWNTs and their Raman spectra recorded with multiple excitations (785nm, 633nm, 532 nm and 488 nm) are shown in Figure 3.8. It was noticed that, although the growth conditions such as temperature, plasma power, and pressure were properly modulated for growth of SWNTs, the CNTs grown with H₂/C₂H₄ ratio of 20 sccm/40 sccm are mixture of SWNTs and few walled CNTs, indicating proper H₂/C₂H₄ ratio is another important factor for growth of SWNT in addition to the alleviation of ion bombardments.

Due to the resonance nature of Raman signals from SWNTs, the RBM in Raman spectra can be used to assign and evaluate metallic and semiconducting SWNTs according to the well known Kataura's plot [16]. For example, the RBM recorded with a 785 nm excitation show extensive signals of semiconducting SWNTs (s-SWNTs) since the Hove electronic transitions in semiconducting SWNTs are resonant with this particular excitation if the diameters of the SWNTs are in the range of 0.7-1.5 nm [50-52]. In Figure 3.8 (a), the RBM frequency regions characteristic for metal or semiconductor SWNTs are highlighted based on Kataura's plot. For 633 nm excitation, RBM signals in the regions of 160-225 cm⁻¹ originate from the van Hove electronic transitions of metallic SWNTs (m-SWNTs), while other regions are associated with s-SWNTs [50,51]. For 532 nm and 488 nm excitations, the RBM signals < 225 cm⁻¹ are assigned to s-SWNTs

[50,52]. As introduced in chapter 2, the G band can also be used to distinguish between metallic and semiconducting SWNTs. Due to the strong electron-phonon coupling of G-band in m-SWNTs, G- band is significantly softened to 1550 cm^{-1} and shows a broad Breit-Wigner-Fano (BWF) feature [16].

Figure 3.8 Raman spectra of VA-SWNTs synthesized at 600°C , 15W, 3 Torr with varying $\text{H}_2/\text{C}_2\text{H}_4$ ratio. (a) 30 sccm/30 sccm, (b) 40 sccm/10 sccm, and (c) 40 sccm/5 sccm.

The Raman spectra of different excitations indicate that the SWNTs synthesized with $\text{H}_2/\text{C}_2\text{H}_4$ ratio of 30 sccm/30 sccm are mixture of m-SWNT and s-SWNT and the

diameters of the as-synthesized SWNTs are in the range of 1-2 nm. The apparent BWF peaks from m-SWNTs were probed by both the 633nm and 532nm excitations. Some Raman spectra of 633 nm excitation showed extremely strong RBM signals from m-SWNTs [16]. Moreover, it seems that the D band originated from m-SWNTs is stronger than those of s-SWNTs. When the H_2/C_2H_4 ratio was reduced to 40 sccm/10 sccm, the m-SWNTs coexist with s-SWNTs, but the strong RBM signals from m-SWNTs cannot be found, indicating the reduced fractions of m-SWNTs caused by selective etching. If the H_2/C_2H_4 ratio was further reduced to 40 sccm/5 sccm, there are no apparent changes in RBM regions, however the D band intensity in Raman spectrum of 785 nm excitation increase, indicating etching of s-SWNTs by redundant H radical. Therefore, H_2/C_2H_4 ratio in plasma also has strong influence on the structure of as-grown SWNTs.

3.3 Synthesis of linear carbon chains encapsulated inside single-walled carbon nanotubes (C_n @SWNTs)

3.3.1 Synthesis of C_n @SWNTs by plasma-enhanced chemical vapor deposition

With optimized synthesis parameters, VA-SWNTs can be synthesized on Si wafers in large scale, as demonstrated in Figure 3.9. In order to grow VA-SWNTs on cheap and conductive substrates, such as aluminum (Al) foils used in kitchen, we have developed a large area dip-coating method based on the wet chemical catalyst procedure according to Maruyama *et al.* [30]. Briefly, cobalt acetate and iron acetate salts were dissolved in ethanol to give metallic concentrations of 0.05 wt% and the weight ratio of Co:Fe is kept at 1:1. The Al foils with thickness of $\sim 15 \mu m$ were preheated at 500 °C for 5 min in air before dip-coating. The Al foils were drawn from the Co-Fe ethanol solution at

a speed of 4 cm/min and then calcined at 500 °C for 1 min. Freshly deposited Co-Fe catalysts were used immediately for synthesis of SWNTs. Due to the limited melting point of Al foils, the growth temperature was set at 500 °C. Once the synthesis temperature was reached, the hydrogen plasma was ignited to pre-treat the Co-Fe catalysts for 1 min at 10 W, 1 Torr. Subsequently, the plasma power was reduced to 5 W, and C₂H₄ was introduced at a flow rate of 20 sccm for 5 min growth, while the H₂ flow rate was maintained as 30 sccm.

Figure 3.9 *Photographical image of the as-synthesized VA-SWNTs on a 6 inch Si wafer.*

Figure 3.10 *SEM image of VA-SWNTs synthesized on Al foil with Co-Fe catalyst.*

Figure 3.10 shows a SEM image of the as-synthesized VA-SWNTs on Al foil with dip-coated Co-Fe catalyst. The length of the VA-SWNTs is around 2~3 μm . Raman spectroscopy characterization of the as-synthesized VA-SWNTs was carried out using four laser excitations of 514 nm (2.41 eV), 532 nm (2.33 eV), 633 nm (1.96 eV), and 785 nm (1.58 eV). Spectra taken at various locations on the substrate are essentially identical, showing uniform distribution of the SWNTs throughout a fairly large area of ~15 mm x 40 mm. Figure 3.11 displays the representative Raman spectra of the VA-SWNTs recorded by different laser excitations. A sharp but split G band and a weak D band at 1300-1350 cm^{-1} are observable in all the four spectra while the RBM bands are located at different wave numbers between 150 and 400 cm^{-1} . According to formula $\omega_{\text{RBM}} (\text{cm}^{-1}) = 243/d_t (\text{nm}) + 10$ [16], the diameters of the SWNTs are distributed from ~ 0.63 to 1.3 nm. Of particular interest is the RBMs observed using the 785 nm (1.58 eV) laser excitation, which exhibit a sharp peak at ~370 cm^{-1} , and using the Kataura plot we can attribute the RBM at 370 cm^{-1} to zigzag (8,0) SWNTs with diameter of 0.63 nm [16].

Small intensity features were also observed at ~1732 cm^{-1} and 1938 cm^{-1} , respectively. They are respectively known as M band, the overtone of out-of-plane mode at 834 cm^{-1} , and iTOLA, the second-order combination mode of the in-plane tangential optical phonon [16]. Under a 785 nm laser excitation, there are two intense bands at ~1770 and 1860 cm^{-1} . Such strong Raman bands should not be attributed to the combinational modes (M and iTOLA) because resonant Raman scattering studies of SWNT bundles [53] and individually suspended SWNTs [54] indicate the combinational modes have much lower intensities than the first-order G bands. Furthermore, the intense bands are only observable under a 785 nm Raman laser excitations. Theoretical studies of

C_n @SWNTs revealed that the linear carbon chain exhibited length-dependent stretching modes (ω_s) around 1850 cm^{-1} [55]. Liu *et al.* [55] predicted that the stretching mode of C_n @SWNT is $\sim 1790\text{ cm}^{-1}$ for $n = 2$, while $\omega_s \sim 1850\text{ cm}^{-1}$ for $n = 14$. Similarly, Kurti *et al.* [56] predicted the stretching mode of C_n @SWNTs is $\sim 1795\text{ cm}^{-1}$ for $n = 75$, while $\omega_s \sim 1870\text{--}1877\text{ cm}^{-1}$ for $n = \infty$. Thus we would like to assign the bands at $\sim 1770\text{ cm}^{-1}$ and 1860 cm^{-1} (labeled as L bands in Figure 3.11) to the stretching modes of short and long linear carbon chains respectively. The linear carbon chains encapsured in SWNT was indeed observed under HRTEM. For example, Figure 3.12 clearly shows the existence of short (1-2 nm) carbon chains inside a SWNT, as indicated by the red arrows.

Figure 3.11 Raman spectra of VA-SWNTs synthesized by Co-Fe bimetallic catalyst support on Al foils using four different laser excitations.

Figure 3.12 HRTEM image of C_n @SWNT.

To further understand the L bands of C_n @SWNTs, we had measured Raman spectra at variable temperatures. A Linkam cell (Linkam TS600) was used for variable temperature Raman spectroscopy with 785 nm laser excitation. A low laser power of ~1 mW was used to avoid laser heating and the spatial resolution of the Raman instrument (Renishaw inVia Raman) is 1 cm^{-1} . Figure 3.13 shows G band, D band, and L bands of C_n @SWNTs at three different temperatures. In general, we observed a downshift of G band, D band, and L bands of C_n @SWNT as the temperatures were varied from 80 K to 603 K. The temperature coefficient of the G band, D band, and L bands (1860 cm^{-1} only) are approximately -0.0112 , -0.0092 , and $-0.01312\text{ cm}^{-1}/\text{K}$ respectively. Our variable temperature Raman study of G band was consistent with previous Raman study on arc discharge synthesized SWNT bundles with increasing temperatures [57]. At 80 K, Figure 3.13 (b) clearly distinguishes the L bands from the M and iTOLA bands. The two shoulders of the L bands located at 1735 cm^{-1} and 1910 cm^{-1} should be attributed to the M and iTOLA of SWNTs. Noteworthy, two extra weak Raman peaks at ~ 2050 and 2170

cm^{-1} , which cannot be attributed to combinational modes of SWNT, are also observed at 80 K. Based on the Raman spectroscopy study of C_n @SWNTs samples in next section, these weak Raman should be assigned to the stretching modes of H-terminated carbon chains inside SWNTs.

The Raman band intensity is known to be sensitive to the electronic structures of carbon materials according to resonance effect, and hence sensitive to the laser excitation energy. The enhancement of the L bands observed only at 785 nm (1.58 eV) clearly shows that this resonance should be associated with the intrinsic transition of the linear carbon chains. Density functional calculations of HOMO-LUMO gaps of linear C chains consisting of ~5-51 carbon atoms demonstrated decreasing gaps from 3 eV to 0.5 eV with increasing carbon chain length [58]. The resonance value 1.58 eV here is in a good agreement to the HOMO-LUMO gaps of linear C chains consisting of ~10-20 carbon atoms (~ 1-2 nm in length) [58].

Figure 3.13 (a) G and D bands, and (b) L bands of C_n @SWNTs at three different temperatures using 785 nm Raman laser wavelength.

3.3.2 Synthesis mechanism of C_n@SWNTs

Encapsulation of linear carbon chains encapsulated within MWNTs (C_n@MWNTs) had been observed previously in samples synthesized by arc discharge [59]. These samples exhibit a unique Raman band at $\sim 1850\text{ cm}^{-1}$ [59]. HRTEM reveals a long linear carbon chain (carbon nanowire composed of ~ 100 carbon atoms) has been inserted inside the innermost nanotube of diameter $\sim 0.7\text{ nm}$ [59]. At present, there is no clear understanding of the mechanism of encapsulation of linear carbon chains inside carbon nanotubes. It has been suggested that for C_n@MWNTs, the coaxial concentric SWNTs are likely to form from outside to inner layers. When the innermost nanotubes of diameters $\sim 0.7\text{ nm}$ are formed, it cannot accommodate any more nanotubes due to the restriction of the van der Waals distance of carbon and hence only linear carbon chains are synthesized within the innermost nanotubes [59]. DFT calculations [55] also revealed that linear carbon chain can be energetically inserted along the tubular axes of SWNTs of diameters $\sim 0.7\text{ nm}$.

Since our C_n@SWNTs were synthesized via PECVD, the role of carbon plasma must be important to the formation of linear carbon chains. Molecular dynamics simulations of carbon plasma suggested that *sp* linear carbon clusters exist as metastable species which evolve via cluster-cluster collisions and coalescence to form *sp*² cagelike nanoparticles, fullerenes and carbon nanotubes [60]. The *sp-sp*² transition greatly depends on the conditions of the carbon plasma such as temperatures and density and classifies the transitions into three possible scenarios [60]. Firstly, for high temperature and low-density carbon plasma, the preferred structures are metastable *sp* chains or rings. Secondly the *sp-sp*² transition is enhanced under high density carbon plasma whereby the

sp carbon clusters undergo multiply collision, and eventually cross-link to form fullerene-like cage of sp^2 network containing even number of carbon atoms. Thirdly, for carbon plasma with low temperature and density, a graphitelike flat sp^2 network is observed and some *sp* chains still remain and play the role of defects connecting neighboring graphitelike fragments. The metastable *sp* chains can survive for a longer time period. For example, Milani *et al.* [61] employed a special plasma sputtering technique such that the plasma temperature can be kept as low as 100 K and deposit *sp-sp*² amorphous carbon. The *sp* carbon chains can be stabilized in a sp^2 carbon matrix and used to control the electrical properties of the hybrid material. Thus the likely scenario for the growth of VA- C_n @SWNTs is due to the employment of low substrate temperature (500 °C) and plasma power (5 W). We have used a K-type thermocouple to measure that temperature of the plasma and there is no plasma heating effect at 5 W so that the formation of *sp* linear carbon chains might be generated in the plasma. Thus a fraction of *sp* carbon chains were encapsulated inside as the SWNTs were catalytically synthesized in the alleviation of ion bombard effect.

Our experiments revealed that the flow rate ratio of hydrogen to ethylene was also crucial to the synthesis of C_n @SWNTs. Figures 3.14 (a) and (b) show the Raman spectra of C_n @SWNTs synthesized using 40 sccm H₂/20 sccm C₂H₄ and 40 sccm H₂/10 sccm C₂H₄, respectively, both being taken under 785 nm laser excitation. The L bands are seen to extend to 2000-2400 cm⁻¹ region with increasing hydrogen concentration in the PECVD chamber. We had fitted the L bands using Gaussian peaks according the analysis of Milani *et al.* [61]. We proposed that there are essentially two different types of linear carbon chains. The sharp and intense L bands at ~1760-1850 cm⁻¹ region (as indicated as

blue lines in Figure 3.14) were mainly due to the presence of pure *sp*-hybridized linear carbon chains without end H-terminals. For pure *sp*-hybridized linear carbon chains, there is a structure transition from essentially nonalternating cumulenic structures $(=C=)_n$ for short chains to bond length alternating acetylenic structures $(-C\equiv)_n$ for long chains [62]. Actually, according to Peierls distortion, acetylenic structures are more stable in forming energy than cumulenic structures for infinite long carbon chains [62]. The short carbon chains encapsulated in SWNTs should be in the form of cumulene.

On the other hand, the broad L bands at higher wavenumber regions $\sim 1900\text{-}2300\text{ cm}^{-1}$ (as indicated as green lines in Figure 3.14), were mainly due to H-terminated linear carbon chains. For these H-terminated linear carbon chains, we had further assigned the L bands into H-terminated polyynes ($\sim 2150\text{ cm}^{-1}$) and H-terminated cumulene (1980 cm^{-1}) carbon chains [61]. The peak-fitted Raman positions of the H-terminated polyynes and cumulene encapsulated within SWNT agreed well with the Raman signals of *sp*-hybridized carbon chains with end capped in *sp*²-amorphous carbon matrix [61, 63]. The peak-fitting analysis was also consistent with our synthesis conditions whereby the presence of higher hydrogen concentration gave rise to the formation of H-terminated linear carbon chains. Obviously the higher hydrogen concentration during the synthesis of SWNTs leads to the formation of H-terminated linear carbon chains.

We had also investigated the effects of catalysts on the encapsulation of linear carbon chains within SWNTs. When we replaced the Co-Fe with Co-Ni catalysts, we did not observe the intense L bands from the Raman spectra (see Figure 3.15) of the as-grown SWNTs samples. The deposition of these catalysts was carried out via dip-coating method in the same fashion as the Co-Fe catalysts and the synthesis condition for SWNTs

was also identical (30 sccm H_2 /20 sccm C_2H_4). Thus the combination of Fe and Co in the bimetallic catalyst seems to be essential for the encapsulation of linear carbon chains within SWNTs in our PECVD process. The catalyst effects should be studied in details by both experimental and theory calculation in future work.

Figure 3.14 Gaussian-fitted (a) L bands of C_n @SWNT synthesized with 40 sccm H_2 /20 sccm C_2H_4 , and (b) L bands of C_n @SWNT synthesized with 40 sccm H_2 /10 sccm C_2H_4 . The insets are the RBM peaks of as-synthesized C_n @SWNTs.

Figure 3.15 Raman spectra of SWNTs synthesized using Co-Ni catalysts.

3.3.3 Transport properties of C_n @SWNTs

First principle calculations [64] predicted that, due to the charge transfer between SWNT and carbon chain, the presence of a carbon chain inside a SWNT increases the density of states at Fermi level, which enhances the conductivity of metallic SWNTs and transforms semi-conducting SWNTs to metallic SWNTs. Thus the SWNTs encapsulated with carbon chains is a one dimensional conductor. We also calculate the electronic properties of C_4 @(8,0)SWNT using density function theory based on the Dmol³ code (Accelry Inc V4.3). The energy gap of pristine SWNT (8,0) is determined to be ~ 0.65 eV within GGA-BLYP calculations. Figure 3.16 shows the density of states (DOS) of (8,0) SWNT and C_4 @(8,0)SWNT, which clearly demonstrates that the encapsulation of linear carbon C_4 shifts the electronic band upwards by ~ 0.45 eV and new DOS are created at the vicinity of the Fermi level, and hence converts a semi-conducting (8,0) SWNT into metallic one.

Figure 3.16. Density of states (DOS) of pure (8,0) SWNT and C_4 @(8,0) SWNT.

Using ac dielectrophoresis method we placed a bundle of C_n @SWNTs with a bundle diameter less than 10 nm (confirmed by Raman spectrum) on top of predefined Au/Ti electrodes with 1 μ m separation (see Figure 3.17 (a) upper inset) [65], and studied their charge transport characteristics at 20~400 K. The as-grown C_n @SWNTs were scratched off from the substrates and then dispersed in an aqueous solution with surfactant (1 wt% SDBS) followed by ultrasonic agitation for 2 h. The well dispersed C_n @SWNTs suspension was dropped onto Au (40 nm) /Ti(10 nm) electrodes prestructured on *p*-type silicon substrates with 500 nm SiO_2 . The electrodes of Au/Ti were prepared using standard UV lithographic and liftoff processes. An ac voltage with a 6 MHz frequency was then applied across the electrodes and the peak-to-peak voltage was 6 V. Due to an induced dielectrophoretic force by the applied ac electric field, the C_n @SWNTs in the suspension aligns with the electric field direction and move towards the electrodes [65]. Confirmation for bridging C_n @SWNTs between the electrodes can be done by monitoring the resistance across. The SWNT bundles with diameter less than 10 nm were selected by AFM characterization for the subsequent transport characteristics measured using a HP semiconductor analyzer 4156B at 20K~400 K.

The I_{sd} - V_{sg} curve presented in Figure 3.17 (a) shows that C_n @SWNTs behaves as a metal at room temperature (300 K) as no gate dependence is observed. When the temperature is raised to 400 K, a linear electrical conductance can be clearly observed in Figure 3.17 (b). While nonlinear electrical conductance in C_n @SWNTs is observable at room temperature, and the I_{sd} - V_{sd} curves become highly nonlinear with decreasing temperature. The electrons in C_n @SWNT, a one-dimensional metal as predicted, should be described by Luttinger liquid model, in which the energy states of electron above the

Fermi surface are collective modes arising from electron-electron interaction and cannot be occupied by an individual electron [66-68]. The tunneling conductance through an energy barrier into a Luttinger liquid is predicted to depend on powers of temperature and bias voltage [66-68]. The characteristic power-law dependent tunneling conductance was indeed obtained by analysis of the data demonstrated in Figure 3.17 (b).

Figure 3.17 (c) shows conductance ($G = I_{sd}/V_{sd}$) measured at constant small bias ($V_{sd} = 10$ mV) as a function of temperature (T) on a double logarithmic scale. The data in Figure 3.17 (c) can be fitted with two straight lines in two temperature regions. The linear fitting (blue solid line) between 100 and 300 K means the conductance power law dependence of temperature, $G \sim T^\alpha$. At lower temperatures ($T < 100$ K), the fitted green dash line implies the Coulomb blockade region [66], which will be discussed later. According to the Luttinger liquid model in a tunneling regime, the bias voltage dependent transport current, $I(V)$, has a transition between an Ohmic behavior, i.e., $I \sim V$ in the low bias regime, and a power-law behavior with an exponent β , i.e., $I \sim V^{1+\beta}$ in the high bias regime [66-68]. Figure 3.17 (d) shows $I(V)$ data on a double logarithmic scale with the applied bias voltage ranging over more than 2 orders of magnitude at different temperatures. A transition between Ohmic and power-law behavior is observed as V increases and the curves at different temperatures have a trend to fall onto a single curve at high bias regime. Figure 3.17 (e) shows the curves plotted as $I/T^{1+\alpha}$ vs. $eV/k_B T$ in log-log scales at several temperatures between 100 and 300 K. All the curves at various temperatures merge into a single master curve, well in agreement with the prediction that the power-law behaviors in T and V can scale $I(V, T)$ into a single curve based on the following equation [66-68]:

$$\frac{I}{T^{1+\alpha}} = C \sinh\left(\gamma \frac{eV}{K_B T}\right) \left| \Gamma\left(1 + \frac{\beta}{2} + i\gamma \frac{eV}{\pi K_B T}\right) \right|^2 \quad (3.3)$$

where $\Gamma(x)$ is the complex gamma function, C is a proportionality constant.

Figure 3.17 (a) I_{sd} vs V_{sg} at $T = 300$ K with $V_{sd} = 0.1$ V. Inset are the AFM image of the device and an illustration of the device structure. (b) I_{sd} vs V_{sd} curves in steps of 5 mV at $V_{sg} = 0$ V and temperatures ranging from 20 up to 400 K. (c) Conductance vs T at $V_{sg} = 0$ V and $V_{sd} = 10$ mV. The blue solid line is power-law fits to the data ($G \sim T^\alpha$). The green dashed line indicates the region where the Coulomb blockade becomes important. (d) I_{sd} vs V_{sd} curves between 20 and 400 K. Curves with temperature below 300K show obvious change from linear response to power-law dependence ($I \sim V^{1+\beta}$) at a temperature dependent bias voltage. (e) $I/T^{1+\alpha}$ vs $eV/k_B T$ at temperatures ranging from 100 up to 300 K. The measured exponents are $\alpha = 1$ and $\beta = 0.8$. (f) Coulomb oscillation at 40K: I_{sd} vs V_{sg} curves with different bias.

The green dashed line of conductance vs. temperature between 20 and 100 K in Figure 3.17 (c) indicates the region where the Coulomb blockade becomes important. Figure 3.17 (f) displays clear Coulomb oscillation at 40K by plotting I_{sd} vs. V_{sg} curves with a series of different bias voltages. The device configuration as schematically shown in lower inset of Figure 3.17 (a) is a typical tunneling junction, consisting of two conducting electrodes and a C_n@SWNT bundle across them. The current flow through the tunnel junction in Figure 3.17 (f) is a series of one electron tunnels. Since the C_n@SWNT bundle has very small self-capacitance C, the voltage $\Delta E = e/C$ built up by a tunneling electron can be large enough to prevent another electron from tunneling. The electrical current is then suppressed at low bias voltage $V_b < e/C$. On one hand, if a bias voltage $V_b > e/C$ is applied to the system, electron may tunnel across it and there will be a current flow, which is proportional to the bias voltage [69, 70]. On the other hand, the

electrical potential of the sample can be tuned by the gate voltage. In the blocking state all energy levels of the system, which are accessible to electrons on the source, are occupied. A positive gate voltage, V_{sg} , can lower the energy levels and lead to tunneling [69, 70]. An electron occupies a previously vacant energy level and from there it tunnels onto the drain electrode [69, 70]. Thus, tunneling current fluctuation can be observed at low bias voltages ($V_b < e/C$) with a ΔV_{sg} . In Figure 3.17 (f), the ΔV_{sg} is around 2 V and ΔE is around 9~10 mV.

3.4 Conclusion

- (1) Large scale synthesis of VA-SWNTs by PECVD with the catalyst substrates directly exposed to discharge sheath was achieved at low temperature, 500 °C. For growth of high quality VA-SWNTs at low temperature, it is crucial to alleviate the undesirable ion bombardment etching effects by the optimization of plasma input power and gas pressure.
- (2) The resistibility of as-synthesized VA-SWNTs against ion bombardment etching was found to be proportional to the growth temperature. At relatively low temperature (500 °C), VA-SWNTs were very susceptible to ion bombardments, which could induce structural defects, and even resulted in a structural transition to few-walled nanotubes.
- (3) In capacitively coupled radio frequency PECVD operating at moderate gas pressure, the ion flux, which is significantly dependent on the plasma powers and pressures, is found to be the determinant factor of the ion bombardment etching effect in growth of SWNTs, whereas the energy of ion bombardment applied on the as-grown VA-SWNTs varies in very small range with different process parameters.
- (4) Selective etching of small diameter SWNTs and metallic SWNTs was observed in

PECVD process with increasing plasma power and H_2/C_2H_4 flow rate ratio. With alleviated ion bombardment, if the H_2/C_2H_4 flow rate ratio is smaller than 1, there is also a structural transition from SWNT to few-walled nanotubes.

(5) With special Co-Fe catalyst, linear carbon chains encapsulated in SWNT, C_n @SWNT, had been synthesized for the first time in a well controlled and effective manner using low-power PECVD at low temperature.

(6) The characteristic Raman bands of C_n @SWNT, L bands, shows resonant feature with 785 nm (1.58 eV) Raman laser excitation, since the HOMO-LUMO gaps of the linear C chains lies in the near infrared range. The temperature coefficient of the L bands (1860 cm^{-1} band) is approximately $-0.01312\text{ cm}^{-1}/K$.

(7) Tunneling conductance into C_n @SWNT exhibits power-law dependence on both the temperature and the bias voltage in a wide temperature range from 100 to 300 K, indicating C_n @SWNT is a one dimensional quantum wire described by Luttinger-liquid model. At temperatures below 100 K, coulomb blockade plays role in charge transport of C_n @SWNT.

Chapter 4

Controllable Synthesis and Doping of Graphene Layers

4.1 Introduction

The novel physical properties of single layer graphene (SLG), such as the anomalous quantum hall effect and ballistic transport of the massless Dirac fermions, are closely related to the unique linear energy-momentum dispersion in its electronic bands [1]. In addition to SLG, bi-layer graphene (BLG) is another fascinating system which demonstrates tunable electronic band structures with different stacking orders, i.e. rotation angles between two graphene layers [7,8]. As the most energetically preferred commensurate stacking order, BLG in AB (Bernal) stacking, whose structure has been introduced in chapter 1, has strong interlayer coupling, which splits the π electron linear dispersion into two parabolic branches near the K point [1]. The AB stacked BLG shows a remarkable ability to tune band gap in the band structures and the electron-phonon interactions by a perpendicular electric field effect [71,72].

Large scale growth of SLG by thermal CVD method has been well developed by Li *et al.* [25]. However, CVD synthesis of BLG is still a challenging. In this chapter, synthesis of BLG homogeneously in large area by thermal CVD is explored and the stacking order in CVD BLG was intensively investigated.

As the neighbors of carbon (C) in the periodic table, boron (B) and nitrogen (N) are the dopants mostly studied for carbon materials [18, 73, 74], which would provide p- and n-doping, respectively. Theoretic studies show that the B/N substitutional doping can

modulate the band structure of graphene without impeding its good conducting behavior [75]. The deliberate introduction of these dopants into graphene could offer a possible route to tailor its electronic band structure, which is of great technological importance for its potential applications in nanoelectronics, nanophotonics, sensor devices, and green energy technology. In the third section of this chapter, the N doping of single layer graphene is explored with ammonia (NH_3) gas as the N source.

4.2 Synthesis and transfer of single layer graphene

Large scale synthesis of SLG on copper (Cu) foils by a low pressure CVD (LPCVD) method, which has been introduced in chapter 2, has recently attracted great attention as it provides promising potential for application of graphene [25]. In our lab, we had set up a LPCVD (from Hefei Kejing Company, China) for growth of graphene, which is shown in Figure 4.1 (a). It is a split tube furnace with a quartz tube of 50 mm outer diameter, and the chamber pressure can be controlled in the range of 1~10 Torr by adjusting either gas flow rate or a ball valve between the quartz tube outlet and the rotary van pump with a pumping speed of $2.3 \text{ m}^3/\text{hour}$. $34 \mu\text{m}$ thick Cu foils with purity of 99.95% (from Goodfellow, UK) was used for growth of graphene. The CVD synthesis process was performed according a time-temperature graph shown in Figure 4.1 (b). After loading the Cu foils into the center of quartz tube, the growth chamber was evacuated to a base pressure of 20 mTorr. In a hydrogen (H_2)/argon (Ar) mixture (10 sccm H_2 /20 sccm Ar), the Cu foil was heated up to 1000°C and then annealed for 30 min. Subsequently, methane (CH_4) gas was introduced for CVD of graphene. For a fixed growth time of 30 min, the optimized H_2/CH_4 flow rates for our furnace are 10 sccm/30 sccm. The samples

were finally cooled down to room temperature under H_2/Ar mixture. Figure 4.2 (a) shows a piece of Cu foil taken out from the CVD reactor and Figure 4.2 (b) shows the SEM image of a graphene film grown across a grain boundary in Cu foil.

Figure 4.1 (a) LPCVD system used for synthesis of graphene, (b) time-temperature curve used in the LPCVD synthesis of graphene.

Figure 4.2 (a) The as-grown graphene on Cu foil surface, (b) a SEM image of the graphene/Cu sample.

The as-grown graphene on the Cu foils can be transferred on to desired substrates using the process illustrated in Figure 4.3 [76]. First, a drop of polymethyl methacrylate (PMMA) diluted in anisole (3 wt %) was dispersed on the graphene/Cu surface and then the PMMA coated samples were baked at 160 °C for 1 min. Subsequently, the Cu substrate was etched using an oxidization etchant, such as 0.2 M $\text{Fe}(\text{NO}_3)_3$ in aqueous solution. Notice that, the graphene on back side of Cu foil can be removed according to the surface tension of water by rinsing the sample in water several times when the Cu was partially etched. The PMMA supported graphene films float on the etchant if the Cu was removed. Using a small container, the PMMA/graphene films were scooped out to de-ionized water for cleaning. Afterwards, the graphene with PMMA coating was transferred onto desired substrates such as SiO_2/Si wafers. After drying, the PMMA film was re-dissolved by diluted PMMA [76], and then washed using acetone and isopropyl alcohol (IPA). Figure 4.3 shows the graphene transferred onto various substrates, including SiO_2/Si wafer, cover glass, glass carbon electrode and optical fiber.

Figure 4.3 Processes for transfer of graphene film.

Figure 4.4 Optical graphs of graphene transferred onto substrates. (a) 285nm SiO_2/Si wafer, (b) cover glass, (c) glass carbon electrode, (d) optical fiber with diameter of 2 μm .

Figure 4.5 (a) Optical image of graphene transferred onto 285 nm SiO_2/Si substrates, (b) Raman spectra of graphene. The inset displays the contrast spectrum of graphene.

Figure 4.6 (a) Optical image of graphene transferred onto 285 nm SiO_2/Si substrates, Raman imaging of (b) G band intensity, (c) G band width and (d) 2D band width (FWHM) of the selected area in (a).

Figure 4.5 (a) displays an optical image of graphene transferred onto 285 nm SiO_2/Si substrate, which indicates the transferred graphene film is continuing and uniform in large area. The Raman/contrast spectroscopy characterization of the graphene sample was performed on a WITEC CRM200 Raman system using a 100x objective lens with a numerical aperture (NA) of 0.95. The excitation source for Raman spectroscopy was a 532 nm laser (2.33 eV) with a laser power below 1 mW to avoid laser-induced

heating. Illumination source for the contrast spectroscopy was tungsten halogen lamp (excitation range from 350 nm to 850 nm). As shown in Figure 4.5 (b), the Raman spectra of graphene display two characteristic SLG Raman peaks at $\sim 1580\text{ cm}^{-1}$ and at $\sim 2670\text{ cm}^{-1}$, corresponding to the G band, in-plane vibration mode, and the 2D band, intervalley double resonance scattering of two TO phonons around the K-point of the Brillouin zone, respectively [40]. The single layer feature of CVD grown graphene was also confirmed by contrast spectrum. The inset of Figure 4.5 (b) displays the contrast spectrum of graphene transferred onto 285 nm SiO_2/Si substrate. The maximum contrast value locating around 560 nm explains the visibility of the graphene layers to naked eyes. The contrast peak value is 0.1, close to the calculation value of that for SLG [22].

Raman imaging was performed to probe the uniformity of the CVD graphene film. The CVD graphene sample was placed on an X-Y piezo-stage and scanned under the illumination of laser light with a step size of 300 nm. Figure 4.6 (b) shows a representative Raman imaging of G band intensity showing the uniform distribution measured in a $9\text{ }\mu\text{m} \times 9\text{ }\mu\text{m}$ area on CVD graphene (the corresponding optical microscope image of the scanned area is shown in Figure 4.6 (a)). Notice that the bright area in Figure 4.6 (b) are caused by the wrinkles formed in the cooling process in CVD [25]. Figures 4.6 (c) and (d) show the Raman imaging of G and 2D band FWHM. The distribution of G and 2D band FWHM are in the ranges of $20\text{--}29\text{ cm}^{-1}$ and $34\text{--}44\text{ cm}^{-1}$ respectively; and the representative values are 20 cm^{-1} and 35 cm^{-1} respectively, indicating high quality of the as-synthesized SLG.

4.3 Synthesis of bilayer graphene

4.3.1 Synthesis of bilayer graphene

It was previously reported by Li *et al.* that growth of graphene on Cu foils was a self-limited process and the as-grown graphene is mainly SLG [25,26]. However, interestingly, with the Cu foils of 99.95% purity, we found that large fractions of BLG can be synthesized when the flow rate of CH₄ was increased. Figure 4.7 (a) shows an optical image of graphene grown with H₂/CH₄ flow rates of 10 sccm/40 sccm, which displays clear contrast difference for two kinds of regions in the graphene sheet, indicating different thicknesses or number of layers. The contrast spectra taken from two representative areas, A and B indicated in Figure 4.7 (a), are shown in Figure 4.7 (b). The peak values of the contrast spectra of the A and B regions are 0.1 and 0.18, respectively, close to the calculation values of those of SLG and BLG. Further increasing the partial pressure of CH₄, for example, changing the H₂/CH₄ flow rates to 5 sccm/50 sccm, the bottom SLG can be fully covered by a second graphene layer. However there are large fractions of multilayer graphene (MLG) formed on the grain boundary of the Cu foils.

Without changing the growth parameters described in section 4.2.1, homogenous BLG can be obtained with prolonged growth time. As described in last section, it took 30 min for the growth of a SLG on the Cu surface. In an additional 180 min CVD process, a second graphene layer can be homogeneously grown on the bottom graphene layer. Figure 4.7 (c) is an optical image of the as-grown CVD graphene layers transferred onto a 285 nm SiO₂/Si substrate, which also shows clear contrast difference for two regions in the graphene sheet. The contrast spectra taken from two representative areas, A and B indicated in Figure 4.7 (c), are shown in Figure 4.7 (d). The peak value of the contrast spectra of the A and B regions are 0.18 and 0.27, respectively, close to the calculation values of

those of BLG and three layer graphene (TLG) [22]. After intensive investigations of the optical images and their corresponding contrast spectra, it is found that 90% area of the as-grown graphene sheet is BLG. The rest 10% is mainly TLG with very small fractions of MLG.

Figure 4.7 (a) Optical image of CVD SLG sheet synthesized with 10 sccm H₂/40 sccm CH₄ for 30 min. (b) Contrast spectra of CVD SLG sheet on 285nm SiO₂/Si substrate. (c) Optical image of CVD BLG sheet synthesized with 10 sccm H₂/30 sccm CH₄ for 210 min. (d) Contrast spectra of CVD BLG sheet on 285nm SiO₂/Si substrate.

In addition to the Cu foil with the purity of 99.95%, Cu foils with the purity of

99.999% and 99.8% (Alfa Aesar, US) were also employed in our CVD process for comparison. It was found that after the growth of SLG on the 99.999% Cu foil within 30 min, the second layer cannot be grown even with a longer additional CVD duration, i.e. more than 180 min. Figure 4.8 (a) shows an optical image of graphene synthesized on the 99.999% Cu with 10 sccm H₂/30 sccm CH₄ at 1000 °C for 210 min, which displays uniform feature of SLG. Raman spectrum of graphene grown for 210 min (see Figure 4.8 (b)) are nearly the same as that of graphene grown for 30 min, displaying typical characteristic Raman bands of the SLG. This result is similar to previous report on the growth of predominant SLG in the pyrolysis of CH₄ and H₂ on Cu foils reported by Li *et al.* [25, 26]. The homogeneous and large area growth of BLG in our CVD process should benefit from the lower purity (99.95%) of the Cu foil, where the dopants or impurities could effectively enhance catalytic performance of Cu surface, which had been proved previously in growth of carbon nanotubes/nanofibers on the Cu catalyst [77].

A CVD process on 99.8% Cu foils at 1000 °C for 30 min leads to the formation of graphene films with large fractions of multilayer graphene (MLG) in a background of SLG and BLG, as shown in Figure 4.8 (c). The fraction and the domain size of the MLG could be significantly enlarged by prolonging growth durations. At 1000 °C, the catalytic activity of the 99.8% Cu is much higher compared to that of a more purified Cu. The kinetic factors such as the surface reaction rate plays a critical role on the uniformity of thickness of CVD graphene layers by limiting the deposition of carbon atoms on Cu surface. Faster surface reaction rate, for example on the 99.8% Cu face, results in the loss of the thickness uniformity in our CVD process, which is consistent with recent kinetic study of CVD graphene grown on Cu foils [78]. Most recently, by careful controlling of

CVD kinetics at a much lower process pressure (0.5 Torr), Lee *et al.* also demonstrated the synthesis of large area BLG on 99.8% Cu foils [79]. Thus, it is clear that appropriate catalytic activity of Cu foils and careful controlling of CVD kinetics are important for homogeneous growth of BLG.

Figure 4.8 (a) Optical image of CVD SLG sheet synthesized on 99.999% Cu foils with 10 sccm H₂/30 sccm CH₄ for 210 min. (b) Raman spectra of CVD SLG synthesized on 99.999% Cu foils. (c) Optical image of CVD graphene layers synthesized on 99.8% Cu foils with 10 sccm H₂/30 sccm CH₄ for 30 min. (d) Raman spectra of graphene layers synthesized on 99.8% Cu foils.

4.3.2 Raman spectroscopy/imaging characterization

Raman spectroscopy has been successfully applied to exploit the number of layers and stacking order [40]. For example, the AB stacked graphene layers demonstrates the split 2D bands, while the turbostratic graphite shows a single and sharp 2D band in Lorentzian lineshape, similar to that of the SLG [40]. Figure 4.9 (a) shows the Raman spectra recorded in the as-grown BLG sheet. The variety of Raman mode features such as the intensity of G mode and the width of 2D appears in the spectra of the different parts of BLG sample. To exploit the details, the Raman images are generated by extracting the Raman intensity of G and 2D bands, the peak position and FWHM of 2D as displayed in Figure 4.10 (a), (b), (c) and (d), respectively. The dark (smaller G band intensity) area in Figure 4.10 (a), labeled as area A is a small domain of SLG identified by a typical Raman spectrum of SLG. The medium contrast (appearing in red) area labeled as area B in in Figure 4.10 (a) dominates the entire as-grown graphene sheet. The corresponding Raman spectrum of this area exhibits comparable intensity of G and 2D bands together with a relatively broader asymmetric 2D peak, a standard Raman feature of BLG [40].

Two small bright (in yellow) areas in Figures 4.10 (a) and (b) are noticed and labeled as area D and E. The spectrum of the former shows a strong and sharp 2D band, which is analogous to that of SLG but with an apparent blue shift (13 cm^{-1}) caused by the reduction of Fermi velocity, the same as the Raman spectrum of the decoupled or weakly coupled BLG previously demonstrated in the CVD grown graphene layers and the mechanically cleaved graphene (MCG) layers in folded configuration [80,81]. The spectrum of the latter has a super strong G band with a I_G/I_{2D} ratio of more than 10, which results from the G band double resonance Raman scattering in BLG with special rotation

angles as demonstrated in our previous work on folded MCG [82]. The D and E type areas are widely distributed in CVD BLG sheet but in very small fractions.

Figure 4.9 (a) Raman spectra recorded in CVD BLG sheet. (b) Fittings of the 2D bands in the Raman spectra of CVD BLG sheet.

Figure 4.10 Raman imaging of CVD BLG sheet. (a) G band intensity; (b) 2D band intensity; (c) 2D band peak position; (d) 2D band width.

According to the double resonance theory, the 2D Raman band reflects the properties of the electronic band structures of graphene layers [40]. Figure 4.9 (b) shows the Raman spectra of the interested areas discussed above in the 2D band range. In contrast to the spectra of area D and E, which present a single Lorentzian lineshape 2D band, the spectrum of area B displays an asymmetry lineshape of the 2D band, which cannot be fitted as one Lorentzian peak but multiple components. It is noticed that in some areas of B region, for example C spot indicated in Figure 4.10 (c), the 2D bands can

be well fitted by four components individually with FWHM of 30~35 cm^{-1} . The intensity of the lowest and the highest frequency sub-bands is weaker, which is well analogous to the split 2D band of AB-stacked BLG [40]. It has been interpreted theoretically that the splitting of 2D peak in AB-stacked BLG originates from the four double-resonance Raman processes, a result of the splitting of electrons dispersion in the valence and conduction bands into two parabolic branches caused by the strong interlayer coupling [40]. Therefore, it is unambiguous that most of the areas in our synthesized CVD BLG exhibit strong interlayer coupling though they might deviate a bit from the exact AB stacked BLG due to very small rotation angles and/or larger interlayer separation.

4.3.3 Static and transient absorption spectroscopy characterization

The electronic structure of the CVD BLG was investigated with the optical absorption spectroscopy in UV-Vis-NIR range. After transfer of graphene layers onto the quartz substrates, UV-Vis-NIR absorption spectroscopy characterization was performed on LAMBDA 950 UV/Vis/NIR spectrophotometer (PerkinElmer, US) in the range of 0.6-5 eV. Figure 4.11 displays the absorption spectra of both the CVD SLG and the CVD BLG for comparison. The absorption spectrum of the CVD SLG shows a broad and asymmetric optical absorption band at 4.6 eV, which significantly red-shift from the theoretic value (5.1 eV) of a symmetric absorption peak arising from the interband transitions in graphene [83]. According to recent calculation, the red shift is owing to the strong resonant exciton effect raised in the two-dimensional semimetals [83]. The transmission at low phonon energies ($0.6 \text{ eV} < E < 2 \text{ eV}$) exhibits a nearly flat absorption spectrum with a frequency independent absorbance of 2.3%, which results from linear

dispersion in the low energy bands of SLG [84].

Regarding to the absorption spectroscopy of CVD BLG, it shows similar excitonic effects as those in CVD SLG, but with a less asymmetric optical absorption band at 4.6 eV. The 0.5 eV red-shift of the absorption peak is close to the predicted value of 0.45 eV in AB stacked BLG [83]. Note that at low excitation energies, as shown in the inset of Figure 4.11, the absorbance of CVD BLG does not persist a expected constant value, for example $2 \times 2.3\% = 4.6\%$, but increases from 3.8% to 6% with increasing photon energy. Such a deviation from the idealized flat optical absorbance should originate from the splitting of electron bands in CVD BLG, since the increased absorbance in IR range with increasing excitation energy has been demonstrated in the calculation of IR absorption in AB stacked BLG [85].

Figure 4.11 UV-Vis absorption of CVD SLG and CVD BLG. The inset shows their NIR absorption.

The electron band structures play an important role in carrier dynamics, therefore the splitting of electron bands in CVD BLG, if there are any, would cause difference in carrier dynamics in CVD BLG and CVD SLG. The carrier dynamics of CVD BLG was investigated by transient absorption ($\Delta A/A$) spectroscopy in comparison to those of the stacked layers of CVD SLG. For pump-probe measurements, the output of titanium-sapphire (Legend Elite, Coherent) regenerative amplifier seeded by an oscillator (Micra, Coherent) was used as a pulse laser source: wavelength 800 nm, pulse width 65 fs, pulse repetition rate 1 kHz, and average power 3.5 W. The main part, 90%, of the radiation was converted into the UV (350 nm) by use of optical parametric oscillator (Topas, Light Conversion) with following second- and fourthharmonic generation that was used as pump pulse. The remaining 10% was used to generate white light continuum in CaF_2 plate, i.e. probe pulse.

The previous carrier dynamics study demonstrated that the stacked CVD SLG layers show layer number independent carrier dynamics and persisted nearly the same carrier dynamics as those in SLG due to weak layer interaction [86]. In this spectroscopy measurement, the CVD BLG and the stacked CVD SLG in two layers on quartz substrates were pumped with the photon energy of 3.55 eV (350 nm) and probed with probe photon energy (E_{pr}) from 1.77 to 2.48 eV (500-700 nm). Figure 4.12 displays the transient absorption spectra of the CVD BLG and stacked CVD SLG layers probed at 2.17 eV (570 nm). According to the previous study [86], the deconvolution-fit processes of kinetic curves resulted in two time components: τ_{rise} within 60 fs, a characteristic ultrashort time limited by the instrument resolution and τ_{decay} in a 100 fs time scale, a carrier relaxation time in agree with those measured in the epitaxial graphene and

graphite [86-88]. The τ_{rise} , a time when the maximum bleaching happens at the probed energy level, originates from intraband hot carrier thermalization governed by the carrier-carrier scattering [86, 88]. Subsequently, these hot carriers relax their energies mainly by the carrier-optical phonon scattering in the decay time of τ_{decay} [86-88]. Note that the τ_{decay} of the CVD BLG is 200 fs, larger than 130 fs of the stacked two layers of CVD SLG. This slower decay time in CVD BLG should originate from the electron band splitting, which will be discussed in details as below.

Figure 4.12 Transient absorption spectra ($\lambda_{\text{excitation}} = 350 \text{ nm}$; $\lambda_{\text{probe}} = 570 \text{ nm}$) of CVD bi-layer graphene and stacked two CVD single layer graphene films on quartz.

Figure 4.13 shows the dependence of the decay times versus the probe photon wavelength. The decay time, for both the CVD BLG and the stacked two layers of CVD SLG, has an increasing tendency with increasing probed photon wavelength, i.e. the

electrons at the lower excited level live longer compared with the ones at the higher energy level, analogous to those in graphite [89]. It is clear that the decay time in CVD BLG are always slower than those in stacked two layer CVD SLG and their discrepancy become larger at lower probed photon energy. Such phenomenon should be caused by slow relaxation time during the interband scattering at the edges of the split electron bands in BLG, which was previously demonstrated in the carrier dynamics of single walled carbon nanotube with split band structures [90].

Figure 4.13 Decay times versus the probe photon wavelength in the range of 500-700 nm. The inset shows the pump/probe configuration in the electronic bands of bi-layer graphene and the interband/intraband decay process.

The inset in Figure 4.13 indicates the split band structures in strongly coupled BLG and the pump/probe related optical transitions. After photo-excitation and rapid thermalization, the relaxation of carriers occurs mainly through intraband carrier-phonon

scatterings in each subband down to their band-edge states on a 100 fs time scale, since the intraband scattering rates is much higher than interband scattering [88]. Eventually, the carriers in upper subband edge will decay to the lower subband by the interband scatterings, which are in picosecond time scale as observed in graphite and single wall carbon nanotube [88, 90, 91]. Such a slow decay time at the upper subband edge will accumulate carriers and slow down the intraband decay in the upper subband according to the density of states effects and Pauli blocking [88]. Obviously, such slow down effect will become more apparent with decreasing energy level, in agreement with our observation. Therefore, consistent with above Raman spectroscopy and NIR absorption spectroscopy investigation, the carrier dynamics study also imply that electronic bands in CVD BLG should be in split form.

4.3.4 Photoelectron spectroscopy characterization

The electronic structure of the CVD BLG was further investigated by photoelectron spectroscopy in comparison of its C 1s core-level and valence bands with those of CVD SLG and highly ordered pyrolytic graphite (HOPG). The photoelectron spectroscopy measurements of the graphene samples were performed on ESCALAB 250 (Thermo VG Scientific). For the XPS analysis, monochromatic Al K α ($h\nu = 1486.6$ eV) excitation was employed. For the UPS analysis, a He lamp with 40.8 eV (He II) excitation energies was used. Figure 4.14 shows the C 1s core-level spectra of CVD SLG, CVD BLG, and HOPG, which are quite similar to each other. The C 1s spectra are fitted with two components: the main peak at a binding energy of 284.4 eV assigned to sp^2 hybridized C atoms in graphene, and another peak at higher binding energy of 285.1 eV

assigned to sp^3 hybridized C atoms, which should result from defects, such as the graphene edges on HOPG formed during mechanical cleavage [92]. The FWHM of the main peaks of CVD SLG, CVD BLG, and HOPG are 0.65 eV, 0.65 eV and 0.6 eV, respectively. Such narrow FWHM of CVD SLG and CVD BLG imply high quality of the as-grown CVD graphene.

Figure 4.14 *C 1s core-level X-ray photoelectron spectra of CVD SLG, CVD BLG, and HOPG.*

Figure 4.15 shows the valence band spectra of CVD SLG, CVD BLG, and HOPG probed by He II excitation. All the valence band spectra show five characteristic states of the graphite, which are assigned to: (1) C 2p π between 0 and 4 eV; (2) the crossing of C 2p π and C 2p σ bands around 5.9 eV (2p $\pi + \sigma$); (3) C 2p σ at 7.9 eV; (4) C 2s-2p hybridized state at 10.6 eV; and (5) C 2s σ band at ~ 13.4 eV [93]. With the increase of graphene layer numbers, there are two apparent differences among the spectra, (1)

narrowing of bandwidth for the $2p \pi$ and $2p \pi+\sigma$ states, and (2) blue shift of $2p \pi$ state and red shift of $2s$ - $2p$ hybridized state in the CVD SLG. The bandwidth of the $2p \pi$ state for the CVD SLG, CVD BLG and HOPG are 1.45 eV, 1.2 eV and 1 eV, respectively.

Figure 4.15 Relative variation of He II UPS valence band spectra of CVD SLG, CVD BLG, and HOPG.

Similar to the previous UPS study of multi-walled carbon nanotubes and graphite, the origin of the UPS bandwidth for graphene should be mainly attributed to the photohole life time broadening and the phonon broadening [94, 95]. Generally, these two broadening mechanism are controlled by the Auger quenching process and hole-phonon coupling, respectively, both of which are determined by the electron band structures and corresponding density of states [96]. Therefore, the bandwidth of CVD BLG in between those of the CVD SLG and HOPG indicates that the electronic structure of CVD BLG

should deviate from that of the CVD SLG and approach that of HOPG, which consist of predominant fractions of AB stacked graphene layers [97]. For better understanding of the electronic structures of our CVD BLG, especially the details in splitting of electron bands due to interlayer interaction, angle-resolved photoemission spectroscopy (ARPES) characterization is required to be performed in future work [98]. Regarding to the binding energy shift of $2p\ \pi$ state and $2s$ - $2p$ hybridized state in CVD SLG, it should result from curvature of the ripple structures in SLG and the corresponding rehybridization of π and σ states, which was previously revealed in multi-walled carbon nanotubes by UPS investigation [95]. On the other hand, there are fewer amounts of ripples in BLG, resulting in little influence on both the atomic and the electronic structures of BLG [20].

4.4 Nitrogen-doping of single layer graphene

4.4.1 Distribution of N in graphene

High quality graphene can grow on Cu foils at relatively low temperature by pyrolysis of H_2 and ethylene (C_2H_4) at low pressure. It was found that growth temperature required for graphene synthesis on 99.95% Cu foils can be reduced to 800 °C. The growth dynamics of graphene on Cu foils with different purities at different growth temperature and partial pressure of C sources would be intensively studied in future work. The N doping of graphene was performed by pyrolysis of H_2 and C_2H_4 in the presence of ammonia (NH_3) at 900 °C. For growth of SLG, the Cu foil was heated up and annealed at 900 °C for 30 min in the flowing 10 sccm H_2 /20 sccm Ar. The gas mixture of H_2 and C_2H_4 was then flowed at 4.6 Torr with rates of 30 sccm and 10 sccm for 30 min, respectively. For growth of N doped graphene, NH_3 diluted in He (NH_3 /He, v/v 10%)

with the flow rate of 3~12 sccm was introduced into the reactor during the graphene growth process without changing the flow rates of H_2 and C_2H_4 .

Figure 4.16 (a) Raman spectrum of the CVD graphene; the inset shows the contrast spectra of the CVD graphene on 285 nm SiO_2/Si substrate. (b) Raman spectra of the CN_x graphene synthesized with the NH_3/He flow rate of 3 sccm (GN3).

Figure 4.16 (a) shows the Raman spectrum of CVD SLG grown at 900 °C. In addition to the characteristic G and 2D Raman peaks, there is a weak peak at 1340 cm⁻¹, which was assigned to D band activated by defects via an intervalley double-resonance Raman process [40]. Commonly the intensity ratio of D band and G band (I_D/I_G) was used to evaluate the defect density in graphitic materials [99]. The small amount of defects in graphene should be formed during the CVD process. The single layer feature of as-grown graphene was confirmed by contrast spectrum [22]. As shown in the inset of Figure 4.16 (a), the contrast value of the graphene transferred onto 285 nm SiO_2/Si is 0.1, close to the calculation value of that for SLG [20].

Figure 4.17 (a) D and (b) 2D band intensity Raman imaging of CN_x graphene synthesized with the NH_3/He flow rate of 3 sccm (GN3); (c) D and (d) 2D band intensity Raman imaging of CN_x graphene synthesized with the NH_3/He flow rate of 6 sccm (GN6). The imaging area is 6 $\mu m \times 4 \mu m$.

The N doping greatly enhances the defect density in graphene as shown by the strong D band in Figure 4.16 (b). By Raman mapping investigation (the sample was placed on an X-Y piezo-stage and scanned under the illumination of laser light with a step size of 250 nm), the distribution of defects (incorporated N) in the N-doped graphene (CN_x graphene) is inhomogeneous. Figures 4.17 (a) and (b) respectively are the D and 2D band Raman imaging of the CN_x graphene synthesized with 3 sccm NH_3/He flow rate (GN3). Both the D and 2D band images are not uniformly distributed but compensating to each other in terms of bright/dark areas, indicating that the defects exist in domains. The A and B spots in the bright D imaging area in Figure 4.17 (a) show strong D and D'

(activated by defects via an intravalley double-resonance process [40]) bands in Figure 4.16 (b), while they are associated with low 2D band intensity (black areas in Figure 4.17 (b)), indicating high defect density, i.e. N rich area. The B area located at the bordering the domains, with much lower different defect density than that in the center of domains. The C type area is dominated in this sample, with nearly the same Raman spectrum of the pristine CVD graphene, indicating no or small amount of N incorporated in such areas.

Figure 4.18 Raman imaging of CN_x graphene synthesized with the NH_3/He flow rate of 12 sccm (GN12). (a) D band intensity, (b) 2D band intensity, (c) G band height, (c) D' band height.

When the NH_3/He flow rate was increased, the Raman spectra corresponding to the A, B, C areas keep nearly unchanged, but the domain size of the A area, i.e. N rich area, increases obviously, as shown in the D and 2D band Raman images (Figures 4.17 (c)

and (d)) of the CN_x graphene synthesized with 6 sccm NH_3/He flow rate (GN6). Figure 4.18 shows Raman imaging of CN_x graphene synthesized with the NH_3/He flow rate of 12 sccm (GN12). The continuous and single layered graphitic structure in N-rich area is evidenced by featureless G band Raman imaging. While all the D, D' and 2D band images demonstrate the domain like distribution of N. Figure 4.19 shows Raman spectra of GN12 taken from the N rich and N free areas, which are quite similar to those in Figure 4.16 (b).

Figure 4.19 Raman spectra of the CN_x graphene synthesized with the NH_3/He flow rate of 12 sccm (GN12). Spectrum (a) and spectrum (b) corresponds to the A and B spots in Figure 4.18, respectively.

The distribution of N in graphene was further investigated by time-of-flight secondary ion mass spectrometry (TOF-SIMS) imaging. TOF-SIMS study of the as-

grown CN_x graphene on Cu foils was performed on TOF-SIMS⁵ (ION-TOF GmbH) using 50 KeV Bi_3^{++} as ion beams. The lateral resolution for SIMS imaging was 100 nm. With the ion beam bombardment on the CN_x graphene sample surface, characteristic mass fragments from the C and CN fractions, including C^- , C_2^- , C_3^- , C_4^- , and CN^- , are demonstrated on the negative ion spectra. The CN^- peak with strong intensity indicates the incorporation of N in the graphene lattice. Similar to the Raman imaging, the chemical imaging generated from the CN^- and the dominated C fraction (C_2^-), as shown in Figure 4.20, clearly show the domain distribution of the N in graphene sheet. Figure 4.21 displays the TOF-SIMS mass spectra in linear scale from the N rich (A spot) and N less (B spot) area. Note that CN^- appears in both spectra. In comparison to the Raman imaging, it seems that there are quite amount of N incorporated into the graphene area where the D band in Raman spectrum is very low.

Figure 4.20 2D TOF-SIMS images of CN_x graphene synthesized with the NH_3/He flow rate of 6 sccm (GN6) generated from the (a) CN^- intensity and (b) C_2^- intensity. The imaging area is $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$.

Figure 4.21 TOF-SIMS mass spectra in linear scale from the A and B spots indicated in the inset. The inset is an overlay imaging of CN^- and C_2^- mass spectra images. N rich area is demonstrated with red color.

4.4.2 Photoelectron spectroscopy characterization

To determine the N/C atomic ratio, bonding configurations of incorporated N and the corresponding electronic structures in CN_x graphene, photoelectron spectra of the CN_x graphene samples were measured. XPS and UPS studies of the as-grown graphene/ CN_x graphene on Cu foils were performed using ESCALAB 250 (Thermo VG Scientific). For the XPS analysis, monochromatic Al K α ($h\nu = 1486.6$ eV) excitation was employed. For the UPS analysis, a He lamp was used with 21.2 eV (He I) and 40.8 eV (He II) excitation energies. Figures 4.22 (a) and (b) respectively are the C1s and N1s

core-level spectra of the CN_x graphene synthesized with 6 sccm NH_3/He flow rate (GN6). The C1s peak can be fitted with two components: the main peak at binding energy (BE) of 284.4 eV (C1) is assigned to sp^2 hybridized C atoms in graphene while another peak located at 285.5 eV (C2) should be assigned to sp^2 C atoms bonded with N [100,101]. Table 1 shows the fitting results for all the graphene/ CN_x graphene samples. At lower N doping level, the C-N peak shifts to 285 eV.

Figure 4.22 (a) C 1s and (b) N 1s core-level X-ray photoelectron spectra of CN_x graphene synthesized with the NH_3/He flow rate of 6 sccm (GN6).

Table 1. Variation of N/C atomic ratio, C 1s/N 1s binding energy and C 1s/N 1s peak width (FWHM) of CN_x graphene synthesized with different NH_3/He flow rates.

NH_3/He Flow (sccm)	0	3	6	9	12
N/C ratio (%)	0	1.6	16	6	2.2
C1s (C1) BE (eV)	284.4	284.35	284.4	284.35	284.35
C1s (C1) FWHM (eV)	0.7	0.7	0.7	0.7	0.7
C1s (C2) BE (eV)	-	285	285.5	285.2	285.1
C1s (C2) FWHM (eV)	-	1.2	1	1.25	1.3
N1s BE (eV)	-	399.35	399.3	399.35	399.4
N1s FWHM (eV)	-	0.8	0.75	0.75	0.75

The binding energy of N1s located at 399.3 eV may originate from sp states of N ($-C\equiv N$, carbonitrile groups) or from sp^2 hybridized N atoms with two sp^2 hybridized C neighbors ($C=N-C$, pyridinic N) with adjacent carbon vacancies [73, 74, 102-104]. Since the C1s corresponding to carbonitrile groups, which is around 286.5 eV [105,106], was not observed in our C1s spectra, we can assign the 399.3 eV peak to pyridinic N. The N1s spectrum is very sharp (FWHM, 0.75 eV), which can only be fitted with one peak component as shown in Figure 4.22 (b), indicating the pure pyridinic N bonding configuration formed in our CN_x graphene samples, since other two possible N bonding configurations, pyrrolic (N incorporated in five-membered heterocyclic ring) and graphitic (or quaternary, sp^2 hybridized N bonded with three sp^2 hybridized C neighbors) N would have greater binding energies between 400.5 and 401.3 eV [73,74,103].

The N/C atomic ratios in CN_x graphene synthesized with different ammonia flow rate are shown in table 1. The N/C atomic ratio reaches its maximum (16%) with the ammonia flow rate of 6 sccm, and then decreases with the increasing of ammonia flow rate. Such a decrease of N/C atomic ratio with the increasing of ammonia flow rate was previously reported in synthesis of N doped carbon nanotubes, which may be caused by the instability of chemisorped N on C at high N radical concentration [107,108]. Since the above measured N/C atomic ratios are an average value over a large probed area (spot size of the X-ray is around 500 μm), the N/C atomic ratio in the N rich area should be even larger.

The valence-band (VB) electronic structure of the CN_x graphene was probed with UPS. Figures 4.22 (a) and (b) show the He II and He I valence band spectra respectively for the CN_x graphene synthesized with different N/C atomic ratios. The pristine CVD

graphene (CVD-G) shows five peaks, which are assigned to: (1) C 2p π between 0 and 4 eV; (2) the crossing of C 2p π and C 2p σ bands around 5.9 eV; (3) C 2p σ at 7.9 eV; (4) C 2s-2p hybridized state at 10.6 eV; and (5) C 2s σ band at ~13.3 eV [93]. After N incorporation with 3 sccm NH_3 /He flow (G900-N3), the He II spectrum remains the same as that of pristine CVD graphene. Upon N incorporation with increasing NH_3 /He flow rate (GN6 and GN9), two distinct features appear in He II spectrum, at approximately 4.9 and 7.2 eV, which appear to originate from N lone pair state (a pair of electrons strongly localized on the N atom) and delocalized C-N 2p π state (C-N π) of the pyridinic N, respectively [104,105,109]. By peak analysis, it is noted that the intensity ratio of the C-N π component and N lone pair component is around 0.9 for the GN6 and GN9 samples, in good agreement to the ratio of two C-N π bonding over two lone-pair electrons in pyridinic configuration. The (C-N/N lone pair) ratio increases to 1.2 for the GN12 samples, indicating the enhancement of C-N π component in the CN_x graphene synthesized with high NH_3 /He flow rate. The N-doping induced features are also observable in He I spectra. Furthermore another extra feature located at 9 eV can be observed in He I spectrum for all CN_x graphene samples, which should be assigned to the C-N σ bonds [109].

The N doping may result in the enhancement of state density near the Fermi level. In both He II and He I spectra, the delocalized 2p π states of GN6 get more pronounced and there appears an additional state at 2.3 eV as a shoulder of the 2p π peak, whereas the delocalized C 2p π states of GN3, GN9 and GN12 show significant depression. Each N atom has five 2p valence electrons vs. four per C atom. The substitution of electron-rich N into the C network in the form of graphitic N would contribute with two electrons to

the π electron system as compared to one π electron per carbon atom. The extra electron may enter the π^* state, giving a “ π doping” effect [73]. The pyridinic N atom is bonded to two neighboring C with forming of C vacancies in the graphene sheet. The two electrons are contributed to the localized N lone pair state, and the pyridinic N only exhibit weak doping effect if next to a vacancy [73]. The pyridinic N incorporation in C network would enhance C-N $2p\pi$ states while depress the C-C $2p\pi$ electron state density, as observed in sample GN9 and GN12. The observation of enhanced C-C $2p\pi$ states in GN6 sample should be attributed to the presence of a shoulder state at 2.3 eV, which may originate from the $2p\pi$ states of the sp^2 C clusters separated by N in the domains with high N/C ratio [73], in analogous to the $2p\pi$ states of C dimer located at about 2 eV [110].

Figure 4.23 Relative variation of (a) He II and (b) He I UPS valence band spectra of CN_x graphene synthesized with different NH_3/He flow rates. The inset of (b) shows low-energy cutoff of the valence band (measured with He I radiation) of graphene and CN_x graphene as a function of kinetic energy relative to the Fermi level. These spectra have been measured with a sample bias of -3 V.

At a high N/C ratio, the doping effect induced apparent change in density of π states near the Fermi level as shown in Figure 4.23 (a), where the Fermi level (E_F) of pristine graphene is located at $BE = 0$ eV, while for CN_x graphene with high N/C atomic ratio (GN6 and GN9), the raising of the state density at $BE = 0$ eV is observable. This is consistent to the results of work function measurements by using biased He I UPS. As shown in the inset of Figure 4.23 (b), the secondary electron tail threshold of the GN6 sample is shifted by 0.2 eV towards lower kinetic energy in comparison to that of pristine CVD graphene (CVD-G), indicative of a reduction in work function by 0.2 eV. Previously, a reduction of work function by 0.5 eV was found in N doped carbon nanotube (CN_xNT , $x = 12$ at %) with high fraction of graphitic N [101].

4.4.3 Electrocatalytic properties of N doped single layer graphene

Both XPS and UPS characterizations confirmed pure pyridinic N-C bonding configuration in our CN_x graphene. N doped graphene layers with nearly pure graphitic C-N bonding was previously synthesized by Wei *et al.* [100]. Note that pure pyridinic/graphitic N have never been reported during N doping of other carbon materials, such as carbon nanotubes, although N doping in carbon nanomaterials have been studied for decades during intensive study of the synthesis technique [18,73,74]. Different C-N bonding configurations in nitrogen (N) doped carbon materials have different electronic structures and therefore different physical and chemical properties [73]. The N doped graphene with only one kind of C-N bonding configuration is an excellent platform for studying doping effect on the physical and chemical properties, such as electron and phonon transport properties, optical properties, and chemical activity.

Recently, N-doped graphene layers were demonstrated as a promising Pt-free catalyst for oxygen reduction reaction (ORR) with high activity and high durability, which can be applied as nonprecious electrodes in polymer electrolyte membrane fuel cells (PEMFCs) and electrochemical biosensors [111,112]. The novel catalytic properties of N doped carbon materials have been attributed to electronic structure changes caused by the N incorporation into the graphitic structure [113]. However, which kind of C-N bonding configurations should be responsible for the enhanced catalytic activity of N-doped carbon materials is under debate [114-117]. Generally, either pyridinic or pyrrolic type N is considered to be responsible for the ORR activity of carbon nanostructures [114]. Since the N doped carbon materials reported previously always contained several kinds of C-N bonding configurations, our CN_x-graphene incorporated with pure pyridinic N would offer a good opportunity to check the ORR activity of the N-C bonding in pyridinic configuration.

For electrochemical measurements, two layers of graphene/CN_x graphene were transferred onto the glassy carbon (GC) disk electrode (5 mm in diameter, Eco Chemie, Netherlands) through the layer by layer transfer method [76]. The (NH₄)₂S₂O₈ (0.1M) was used as Cu etchant to avoid any Fe³⁺/Fe²⁺ contamination. The electrodes were dried at 60 °C for 120 min. ORR voltammograms were recorded using an Autolab potentiostat (Eco Chemie BV) with a three-electrode system in an oxygen saturated 0.1 M KOH (pH 13) electrolyte solution. The graphene/ CN_x-graphene on the glassy carbon rotating disk electrode (RDE) was used as a working electrode, with the rotating rate varying from 250 rpm to 1500 rpm. An Ag/AgCl electrode was used as a reference electrode and Pt sheet was used as a counter electrode.

Figure 4.24 (a) RDE voltammetry curves for the ORR in O_2 saturated 0.1 M KOH at the CVD graphene electrode, CN_x graphene electrodes and Pt disk electrode; the inset shows the enlargement of the curves in range of -0.15 ~ -0.65 V. Electrode rotating rate: 2000 rpm. Scan rate: 0.01 V/s. (b) RDE voltammetry curves for the ORR at the CN_x graphene (GN12) electrode with various rotation speeds; the inset shows the Koutecky-Levich plots for ORR on CN_x graphene (GN12) electrode.

Figure 4.24 (a) displays the ORR polarization curves on CN_x graphene with

different N/C atomic ratios. For comparison, the curves on the pristine graphene (CVD-G) and the Pt disk electrode (Eco Chemie, Netherlands) are also shown. All the graphene samples, with or without N incorporation, show a poor ORR activity with high onset potential (-0.3 V) as compared to Pt disk. Nevertheless the CN_x graphene exhibits somehow enhanced ORR activity with faster increase of current density (j) above the potential of -0.6 V, in the order of $\text{GN12} > \text{GN9} > \text{GN6} > \text{CVD-G}$, as shown in the inset of Figure 4.24 (a). Note that the ORR activity of CN_x -graphene is not proportional to the total amount of the incorporated N. Despite having lower N content, GN12 electrode shows better ORR activity than that of GN6 electrode.

Recent DFT calculation shows that the incorporated N itself is not the active site for ORR, but the C atom adjoining a N atom have a reduced energy barrier to ORR [118]. Doping of electronegative N atoms reduces the electron density of C atoms that bond with N atoms and polarizes the C atoms into $\text{C}(\delta+)$, making it easy for adsorption of the O_2 (O-O) molecule, which is the first step in ORR process [118,119]. Subsequent electron transfer between $\text{C}(\delta+)$ and O-O will result in forming radical anions [118,119]. However, since O_2 molecule have high density of O lone pair electrons, the polarized pyridinic $\text{N}(\delta-)$ with high density of N lone pair electrons, may have higher energy barrier for the O_2 activation caused by the high repulsion interaction with the O_2 approaching to the adjoining $\text{C}(\delta+)$ atoms [119]. Therefore, the balance between the $\text{C}(\delta+)-\text{O}_2$ and $\text{N}(\delta-)-\text{O}_2$ interactions would cause a optimized N concentration for the desired O_2 activation.

Figure 4.24 (b) shows the RDE voltammograms of oxygen reduction on GN12 electrode with various rotation speeds (ω). The electron transfer numbers were calculated using Koutecky-Levich equation [120]:

$$\bar{i}^{-1} = i_k^{-1} + i_{lev}^{-1}; \quad (4.1)$$

$$i_k = nFK_{O_2}C_{O_2}\Gamma_{catalyst}; \quad (4.2)$$

$$i_{lev} = 0.62nF C_{O_2} D_{O_2}^{2/3} \nu^{-1/6} w^{1/2}; \quad (4.3)$$

$$\bar{i}^{-1} = A + 1/(Bw^{1/2}); \quad (4.4)$$

$$B = 0.62nF C_{O_2} D_{O_2}^{2/3} \nu^{-1/6}; \quad (4.5)$$

where, i is the total current density; i_k is the kinetic current density; i_{lev} is the levich current density; n is the electron transfer numbers; F is the Faraday constant (96500 C mol⁻¹); $\Gamma_{catalyst}$ is the catalyst loading; k_{O_2} is the rate constant for oxygen reduction; C_{O_2} is concentration of O₂ dissolved in 0.1 M KOH solution (1.2 x 10⁻⁶ mol cm⁻³); D_{O_2} is the diffusion coefficient of O₂ in 0.1 M KOH solution (1.9x10⁻⁵ cm² s⁻¹); w is the rotation rate (rad s⁻¹) and ν is the kinetic viscosity of the water (0.01 cm² s⁻¹). The slope of the plot of reciprocal current $\bar{i}^{-1}$ versus the reciprocal square root of rotation rate ($w^{-1/2}$) gives B values. The value of n can be calculated from B by using above parameters [120].

The inset of Figure 4.24 (b) shows the plotting of j^{-1} vs. $w^{-1/2}$. At the potential ranging from -0.4 to -0.6 V, the electron transfer numbers calculated are close to 2, suggesting the 2 electron (2e) reduction pathway in the incomplete O₂ reduction to hydrogen peroxide (H₂O₂). At more negative potentials (< -0.6 V), the H₂O₂ was further reduced to H₂O [120]. Different from the excellent ORR activity with 4 electron (4e) reduction pathway from O₂ directly to H₂O on the N doped carbon nanotubes and graphene layers reported by other research groups [111,113], the ORR activity of our CN_x graphene with 2e reduction mechanism is much lower. In their samples, both of the pyridinic N and the pyrrolic N were incorporated, with binding energies located at 398.3 eV and 400.5 eV, respectively [111,113].

According to intensive X-ray absorption analysis of various N incorporated in carbon nanostructures, Niwa *et al.* found that graphitic N (X-ray absorption peak at 401.5 eV) exhibited a higher ORR activity than that of pyridinic N (X-ray absorption peak at 399.1 eV) [116]. Recently, Nagaiah *et al.* also reported that in N-doped carbon nanotubes, graphitic N played more important role for the enhanced ORR activity in alkaline solution than the pyridinic N [117]. It seems that our result is a more direct support for the observation that C-N bonding in pyridinic configuration may not be an effective promoter for ORR activity. The above-mentioned repulsion interaction between dense lone pair electrons in both pyridinic N(δ^-) and O₂ may be partially responsible for the observed ORR performance of pyridinic N. There are no such dense lone pair electrons in the graphitic N [73]. It is also should be point out that the different ORR performance may also partially result from different binding energies of pyridinic N in different samples, because the reported binding energies of pyridinic N vary in a wide range of 398.3-399.3 eV [103,106,111,112]. Further work in comparing the ORR activity of the graphene samples with pure pyridinic/pyrrolic/graphitic N configurations is needed to clarify the origination of novel ORR activity in N-doped carbon materials.

4.5 Conclusion

- (1) SLG and BLG had been synthesized homogeneously in large area on Cu foil by thermal CVD. The growth mechanism of BLG was found to be related to purity controlled catalytic activity of Cu surface.
- (2) The 2D Raman band of CVD BLG splits into four components, indicating the splitting of electronic bands due to strong interlayer coupling in CVD BLG. The splitting

of electronic bands in CVD BLG is further evidenced by the study of NIR absorption spectroscopy, where interband transitions break down the frequency independent absorption found in SLG. The carrier decay times in BLG probed by transient differential absorption spectroscopy are obviously slower than those of SLG, which is attributed to the influence of slow interband decay in the edges of split electronic bands.

(3) Our results in synthesis and characterization of BLG demonstrated that strongly coupled or even AB stacked BLG would be grown on Cu foils in large area, which is of particular importance for special electronic and photonic device applications based on their split electronic bands.

(4) Nitrogen-doped SLG incorporated with N percentage up to 16% had been synthesized by thermal CVD of H_2 and C_2H_4 on Cu foils in the presence of NH_3 . The Raman spectroscopy and TOF-SIMS imaging show that the distribution of incorporated N in graphene is in domains with size of 1~2 μm .

(5) The pure pyridinic N-C bonding configuration in CN_x graphene was confirmed by the XPS and UPS investigation. Moreover, the UPS investigation demonstrated that pyridinic N efficiently changed the valence band structure of graphene, including the raising of density of π states near the Fermi level and the reduction of work function.

(6) The N doped graphene with only one kind of C-N bonding configuration is an excellent platform for studying doping effect on the physical and chemical properties. Such pyridinic N doping in carbon materials had been generally considered to be responsible for their ORR activity. The 2e reduction mechanism of ORR on our CN_x graphene revealed by RDE voltammetry indicated that the pyridinic N might not be an effective promoter for ORR activity of carbon materials as previously expected.

Chapter 5

Hydrogenation of Graphene: A Case Study of Graphene Derivatives

5.1 Introduction

As introduced in chapters 1 and 2, grafting of hydrogen atoms on graphene has been attracted great attention to exploit their possibilities and efficiency in tuning the electronic band structures of graphene. Different from the hydrogenation of graphene by atomic hydrogen generated from hot tungsten filaments or remote hydrogen plasma [11, 29], an ionic hydrogenation process was developed for the first time in our lab. The ionic hydrogenation is also reversible and the hydrogenation process can be completed in a few minutes, much faster than the atomic hydrogenation process [11]. Moreover, the hydrogenation mechanisms of these two kinds of process are different, leading to significant difference in graphene thickness dependent hydrogenation.

Recent calculations based on density function theory demonstrated that the electronic structures of hydrogenated graphene would show strong dependence on hydrogen coverage [121]. For single side hydrogenation, a band gap insulating behavior was predicted at high coverage [122], while at lower coverage, a localized insulating behavior was predicted and observed at low temperature [11]. Moreover, there is a metal-insulator transition at ultra low hydrogen coverages [123]. Therefore, we present systematic investigations on electronic structure and structural evolution in hydrogenated graphene with different amount of hydrogen coverage on single side by Raman

spectroscopy, XPS, UPS and UV-Vis-NIR absorption spectroscopy.

5.2 Raman spectroscopy study of hydrogenated single layer graphene

5.2.1 Reversible hydrogenation on single layer graphene

Graphene sheets on Si wafer substrates with 285 nm SiO₂ cap layer were prepared by mechanical cleavage from HOPG. Optical microscope was used to locate the graphene samples. The graphene thickness was identified by Raman spectrum and contrast spectrum, which has been described in chapter 2 and 4. Figure 5.1 (a) displays an optical image of a large graphene sheet on SiO₂/Si substrate and Figure 5.1 (b) shows the contrast spectrum recorded from four distinguishing regions marked in Figure 5.1 (a), which indicate these regions are one- to four- layer graphene respectively. The graphene on SiO₂/Si substrates were directly immersed in H₂ plasma for single side hydrogenation. The H₂ plasma was ignited between two metallic parallel-plate electrodes of 20 cm in diameter and 4 cm separation in a capacitively coupled radio frequency PECVD reactor, which had been used for growth of vertically aligned carbon nanotubes in chapter 3. The hydrogen coverage on graphene can be controlled by modulating the H₂ plasma dose with varied parameters such as plasma power, H₂ pressure and process duration. For most of the experiments, the plasma power and H₂ pressure were set as 10W and 1Torr (133Pa), respectively. After hydrogenation, Raman spectra were recorded with different excitation lasers: 2.71 eV (457 nm), 2.54 eV (488 nm), and 2.33 eV (532 nm) with WITEC CRM200 Raman system; 1.96 eV (633 nm) and 1.58 eV (785 nm) with Renishaw inVia Raman system. The laser power on sample is kept below 1 mW to avoid possible laser induced heating.

Figure 5.1 (a) Optical image of graphene sheets on SiO₂/Si substrate; (b) contrast spectrum of one- to four- layer graphene.

Raman spectra of the pristine and hydrogenated graphene under 2.33 eV excitation are shown in Figure 5.2. The Raman spectrum of pristine graphene displays two characteristic peaks, G band at $\sim 1580\text{ cm}^{-1}$ and 2D band at $\sim 2670\text{ cm}^{-1}$. After hydrogenation by H₂ plasma treatment at 10W, 1Torr, 9 min, three defect induced peaks at 1340 , 1620 and 2920 cm^{-1} are observed in the Raman spectrum of hydrogenated graphene (See Figure 5.2), which are assigned to D band activated by defects via an intervalley double-resonance Raman process, D' band activated by defects via an intravalley double-resonance process, and the combination mode of D and G modes (D+G band) respectively [40, 99]. The defects in the hydrogenated graphene result from the formation of *sp*³ C-H bonds as well as the breaking of the translational symmetry of *sp*² C=C network [11]. Commonly the frequency-integrated intensity ratio of D band to G band (I_D/I_G) can serve as a convenient measurement of the amount of defects in graphitic materials [99]. The I_D/I_G of the above hydrogenated graphene is as high as 5, suggesting high defect density induced by hydrogenation [11].

After vacuum annealing (1 Pa) of above hydrogenated graphene at 500 °C for 30 min, almost all of the defect-related Raman bands (D, D', D+G) can be eliminated, as shown in Raman spectrum of dehydrogenated graphene (see Figure 5.2), indicating the defects are mainly sp^3 monovalent hydrogen adsorbates, which can be thermally healed to restore the original graphene lattice. Therefore, similar to the atomic hydrogenation, our hydrogenation of graphene by H_2 plasma is also reversible [11]. Moreover the amount of hydrogen coverage, *i.e.* defect density can be modulated to much larger values than those of atomic hydrogenation [11]. Compared with the initial Raman spectra of graphene, after high temperature vacuum annealing, the intensity of 2D band of graphene decreased and the FWHM of 2D band became broader; moreover, the G and 2D band peaks shows a strong blue shift, which should be attributed to the hole doping by adsorbing oxygen molecular after exposing the annealed graphene to atmosphere [124].

Our capacitively coupled RF hydrogen plasma is operated at moderate pressure (1 Torr) and low power density ($\sim 0.03 \text{ W/cm}^2$). At this highly collisional condition, the ion bombardment energy is in the range of 5 to 15 eV [44, 125]. It is “safe” to expose the graphene sheets directly to H_2 plasma, because the threshold energies for sputtering off carbon atoms in graphite by hydrogen ions was calculated to be about 36 eV [126], which is above the upper limit value for the ion bombardment energy distribution in our H_2 plasma [125]. The ionization rate in capacitively coupled radio frequency H_2 plasma is below 0.1% and the concentration of proton (H^+), H_3^+ and the hydrogen radicals (H atoms) are close to 0.0001%, 0.1% and 1%, respectively [44,125]. Due to the very small fractions of H^+ , we ignore the situation that the energetic proton (H^+) might overcome the energy barrier (3.7 eV) to penetrate the hexagonal carbon network [127]. Therefore, it is

acceptable to assume that the hydrogenation happens only on the top layer of graphene, *i.e.* single side hydrogenation of graphene. Since the hydrogenation by hydrogen radicals/atoms is very slow, for example it takes more than 2 hours in reference 11 to obtain a I_D/I_G of 2, our quick hydrogenation of graphene directly immersed in H_2 plasma should be attributed to the contribution of energetic H_3^+ . Therefore, we can call this kind of hydrogenation process as ionic hydrogenation.

Figure 5.2 Raman spectra of pristine graphene, hydrogenated graphene (10 W, 1 Torr, 9 min) and the dehydrogenated graphene (vacuum annealing at 500 °C for 30 min) excited by 532 nm (2.33 eV) laser.

5.2.2 I_D/I_G saturation effect

In order to investigate the electronic structure and structural evolution in single layer graphene with different amount of hydrogen coverage, graphene samples with

different amounts of hydrogen coverage were prepared by exposure to 10 W, 1 Torr H_2 plasma for different durations. Figure 5.3 shows Raman spectra of single layer graphene treated with 10 W, 1 Torr, 3 min H_2 plasma, using three different excitations. The spectra are normalized respect to the G band intensity. Note that the frequency-integrated intensity ratios of D and G bands (I_D/I_G) are strongly dependent on the excitation laser energy (E_L). The I_D/I_G is 1.6, 3.1 and 6.3 for 2.71, 2.33 and 1.96 eV excitation, respectively, which follows an E_L^{-4} relation. The inverse proportion of I_D/I_G to the fourth power of the laser energy was previously reported in a Raman study of nanographite [128-130]. Based on the calculation of Raman scattering theory [128], matrix elements associated with the double resonance Raman processes of D band show an E_L dependence of E_L^{-4} for grain boundary defects in nanographite.

Figure 5.3 Raman spectra of hydrogenated graphene (10 W, 1 Torr, 3 min) excited by 457nm (2.71 eV), 532nm (2.33 eV) and 633nm (1.96 eV) lasers.

Single layer graphene samples with different amounts of hydrogen coverage were further studied with more Raman excitation energies. The I_D/I_G ratio and I_D/I_G times E_L^{-4} are plotted as a function of hydrogen coverage (or hydrogen plasma treatment dose, defined by $W \cdot \text{Torr} \cdot \text{min}$) in Figure 5.4 (a) and (b), respectively. Under the excitation of 2.71 eV, 2.54 eV and 2.33 eV, the ratio I_D/I_G is firstly proportional to both the hydrogen coverage and the inverse fourth power of the laser energy (E_L^{-4}), but becomes inversely proportional to the hydrogen plasma treatment dose and significantly deviated from the E_L^{-4} relation when the H_2 plasma dose is larger than 90 $W \cdot \text{Torr} \cdot \text{min}$ (stage IV as indicated in Figure 5.4 (a) and (b)). However, in addition to the two increasing and decreasing parts described above, the evolutions of I_D/I_G under 1.96 eV and 1.58 eV excitations show one more part, a saturation stage with no further change for increasing hydrogen coverage. For example, under the excitation of 1.96 eV, the I_D/I_G saturation stage happens when the H_2 plasma dose is between 50 and 90 $W \cdot \text{Torr} \cdot \text{min}$ (stage III as indicated), while the I_D/I_G saturation stage starts at lower H_2 plasma dose (plasma dose ≥ 10 $W \cdot \text{Torr} \cdot \text{min}$, stage II and stage III) when the excitation is 1.58 eV near infrared (NIR) laser. The Raman spectra (recorded under 1.96 eV excitation) of the hydrogenated graphene at each stage were shown in Figure 5.5 (a) for better understanding of this saturation phenomenon. Actually, when the plasma power was set as 15W, the saturation phenomenon was also observed under 2.33 eV excitation, as shown in Figure 5.5 (b). Although the I_D/I_G in Figure 5.5 get saturation, the I_{2D}/I_G keep decrease and the I_D/I_G keep increase with increasing hydrogen coverage. For example, in Figure 5.5 (b), with increasing hydrogen plasma duration, all the I_D/I_G are around 4.9, while the I_{2D}/I_G are 0.2, 0.3, and 0.38 respectively.

Figure 5.4 The evolution of D and G band intensity ratio (I_D/I_G) (a) and $(I_D/I_G) \cdot E_L^4$ (b) with increasing hydrogenation dose in Raman spectra excited by five lasers.

Figure 5.5 (a) Raman spectra (recorded by 1.96 eV excitation) of graphene hydrogenated by 10W 1Torr H₂ plasma for different duration, (b) Raman spectra (recorded by 2.33 eV excitation) of graphene hydrogenated by 15W 1Torr H₂ plasma for different duration.

5.2.3 D band Raman active model

The decrease of I_D/I_G with increasing amount of defects (stage IV here) after an I_D/I_G maximum was also recently reported by Lucchese *et al.* [131] in Raman

spectroscopy investigation of defective graphene induced by Ar^+ ion bombardment, and interpreted by a local active model of D band. In their phenomenological model, the D band in Raman spectra was proposed to be mostly contributed by activation area, i.e. the hexagonal lattices proximity to the defect region, while the defect region, whose radius r_D is around 1 nm (revealed by scanning tunneling microscopy (STM) study), make less contribution to the D band due to strong structural disorder and breakdown of the hexagonal crystalline structure. The size of the activation area is determined by $A = \pi r_A^2 - \pi r_D^2$, where $r_A = r_D + l$, and l is Raman relaxation length for the resonant Raman scattering of D band. The Raman relaxation length l is the average distance traveled by an electron before undergoing inelastic scattering by a phonon, since the phonons of D bands can only become Raman active if the electrons are involved in both the electron-defect elastic scattering and electron-phonon inelastic scattering [132].

Upon increasing the defect density, the corresponding activation areas are created independently from others and eventually overlap, and therefore the D band intensity will reach a maximum when the inter-defect distance, i.e. mean distance between defects, $d = r_A + r_D$. If the defect density is large enough, the activation areas with hexagonal lattice finally shrink, which would significantly reduce the D band intensity. Our case appears to follow this structure evolution trajectory. As revealed by STM investigation of hydrogenated epitaxial graphene grown on SiC substrate [29], the hydrogenation site in graphene still keeps the hexagonal lattice structure after chemisorption of hydrogen dimers. The predicted structural distortion region caused by C-H bonding is in the range of a few atoms around the hydrogenation site, much smaller than 1 nm [121]. Moreover, different from the fixed defect size induced by Ar sputtering, the size of the

hydrogenation site, i.e. r_D , keeps enlarging with increasing hydrogenation coverage, since the hydrogen atoms prefer stick together to form hydrogen clusters [29].

Figure 5.6 Illustration of D band active model with D band Raman relaxation length and photo-excited electron/hole wavelength as critical length scales.

The local active model of D band proposed by Lucchese *et al.* [131] is based on Raman spectroscopy study with a single excitation. The excitation energy dependent I_D/I_G saturation phenomenon observed here implies their model should be revised. The saturation phenomenon can be viewed as an excitation energy dependent I_D/I_G maximum effect. For example, the I_D/I_G maximum value under 1.58-2.71 eV excitations locate at the hydrogenation dose of 10, 50, 90, 90, 110 W*Torr*min, respectively. The origination of this effect should be the fact that D band Raman relaxation length, $l = v_F/(2\gamma)$, shows electron energy dependence [132]. The v_F is Fermi velocity ($v_F = 1.1 \times 10^6$ m/s ≈ 7.3

eV·Å/h in graphene) and the 2γ is inelastic-scattering rate for a photo-excited electron or hole due to phonon emission [132,133]. According to reference 132, $2\gamma = (\lambda_{\Gamma} + \lambda_K)E/2$, where λ_{Γ} and λ_K are dimensionless electron phonon coupling constant, and E is the photo-excited electron or hole energy ($E = E_L/2$). Therefore, $l = 2v_F/[(\lambda_{\Gamma} + \lambda_K)E]$, which implies larger inter-defect distance and lower defect density for the I_D/I_G maximum at lower photo-excited electron energy, in agreement with our observation.

For better understanding of the saturation phenomenon after the maximum point, an illustration for revised D band active model is shown in Figure 5.6 for a clear physics picture. When the inter-defect distance $d > 2r_D + l$, I_D/I_G is proportional to defect density (hydrogen coverage) as each defect site can be a D band activation site. When $\lambda_e < d - 2r_D < l$, where the λ_e is electron wavelength of photo-excited electron or hole and $\lambda_e = v_F/E$, the same photo-excited electron-hole pair can scatter from several defects before recombination and emitting a photon, therefore several defects function like a single defect in electron-defect elastic scattering, a integrant step of D band double resonance scattering process. This situation will lead no significant change in D band intensity with different defect density as what happens for stage II and III in our experiment. When $d - 2r_D < \lambda_e$, the electron simply cannot distinguish between different defects and defects coalesce together to grow up into one big defect in the electron's "eye", thus such "merger of defects" contributes to the decrease of I_D/I_G in stage IV. For the photo-excited electron with lower energy and larger wavelength, the "merger of defects" process is faster, and therefore results in a rapider drop in I_D/I_G , which is consistent with our observation in stage IV. The absence of saturation phenomenon under high excitation energy, for example 2.54-2.71 eV, should result from the fact that in graphene with high

defect density, D band Raman relaxation length l becomes comparable to the electron wavelength λ_e . In pristine graphene, the D band Raman relaxation length l for 0.98 eV electron (633 nm, 1.96 eV excitation, $\lambda_e = 0.745$ nm) is around 3 nm, which was deduced in Raman spectroscopy study of graphene edge [134]. In highly defective graphene, Raman relaxation length l should be much smaller due to significantly reduced Fermi velocity around defect points (smaller than one third of the pristine value) [135].

5.2.4 Structural evolution of hydrogenated graphene

In stage IV, the peak position of G band up-shifts, as shown in Figure 5.7 (a) (recorded using 2.33 eV excitation), while it keeps nearly unchanged at the first three hydrogenation stages. The stiffening of the G band in the fourth stage might be analogous to the phonon confinement as that found in clustering of the sp^2 phase during the amorphization trajectory of graphite [136]. As there is no obvious up-shift of G band in the first three hydrogenation stages, the photo-excited electron and phonon in the hydrogenated graphene should not be strongly confined. At the first three stages, the hydrogen chemisorbed on graphene and form sp^3 C-H bonds, working as point defects distributed randomly in the graphene sp^2 matrix, while at high hydrogen coverage (stage IV in Figure 5.4) the sp^3 C-H bonds start to coalesce and form clusters, as described above, and finally sp^2 carbon domain were encircled within the sp^3 C-H matrix. The coalesced sp^3 clusters work similarly to the one-dimensional defect structure (grain boundary) in nanocrystalline graphite and nanocrystalline graphene which change and cut the long range phonon interaction [130]. Therefore, the electronic structure and phonon dispersion of hydrogenated graphene at the first three stages should be similar to those of

graphene, while they change significantly at high hydrogen coverage (stage IV), which is consistent with the observed deviation of the E_L^{-4} dependence of I_D/I_G at stage IV.

Figure 5.7 (a) The evolution of G band peak position with increasing hydrogenation dose in the Raman spectra excited by 2.33 eV laser; (b) FWHM evolution of D, G and 2D bands with increasing hydrogenation dose in the Raman spectra excited by 2.33 eV laser.

These randomly distributed point defects and coalescent defects also have different influence on the FWHM of D, G and 2D bands, as shown in Figure 5.7 (b) (recorded under 2.33 eV excitation). Unlike the monotonic increase of FWHM of D, G and 2D band with the decreasing crystallite size in nanographite [130], the FWHM of D, G and 2D band of hydrogenated graphene evolves in several stages with increasing hydrogen coverage. At low hydrogen coverage (corresponds to stage I in Figure 5.4), the FWHM of G band increases rapidly with increasing hydrogen coverage, resulting from the decrease of phonon lifetime caused by the increasing probability for the phonon-defect scattering. When compared to the FWHM of the first-order Raman G band, the FWHM of D band are broader due to its double-resonance nature of the scattering

processes in addition to the phonon lifetime broadening, because a range of phonons with different wave vectors is involved in double-resonance scattering [137]. At medium hydrogen coverage (corresponds to stage II and III in Figure 5.4), the FWHM of G and 2D bands increases very slowly with increasing hydrogen coverage and the FWHM of D band keeps nearly unchanged; while the corresponding I_D/I_G in this region increase with increasing hydrogen coverage. The deviation from the increasing tendency of FWHM with increasing I_D/I_G , which was previously demonstrated in Raman spectroscopy study of nanographite, may originate from the different kinds of defects [130]. At high hydrogen coverage stage (stage IV), the FWHM of D, G and 2D bands increases rapidly with increasing hydrogen coverage, because the coalescent defects cut the long range phonon interaction [130].

5.2.5 Electronic structure evolution of hydrogenated graphene

According to the double-resonance nature of 2D and D bands, the excitation energy dependence of D and 2D band peak positions can be used to explore the electronic structures of the graphene around K and K' point [40]. Figures 5.7 (a) and (b) display the excitation energy dependence of D and 2D peak positions, respectively, where the D and 2D bands show linear energy dispersion with rates of around $50 \text{ cm}^{-1}/\text{eV}$ and $100 \text{ cm}^{-1}/\text{eV}$, which are similar to those in graphite [99]. Note that, the energy dispersion rate of D and 2D band peak position for the hydrogenated graphene decrease with increasing hydrogen coverage. For instance, the 2D band energy dispersion rate of graphene treated with $10 \text{ W} \cdot \text{Torr} \cdot \text{min}$ hydrogen plasma dose is around $102 \text{ cm}^{-1}/\text{eV}$, while the energy dispersion rate of the graphene treated with $90 \text{ W} \cdot \text{Torr} \cdot \text{min}$ plasma dose decreased to 92

cm^{-1}/eV . It is also interesting to notice that, with a significant red-shift of D and 2D band peak position for all the excitation energies, the energy dispersion rates of D and 2D band become back to $\sim 50 \text{ cm}^{-1}/\text{eV}$ and $\sim 100 \text{ cm}^{-1}/\text{eV}$ at high hydrogen coverage.

Figure 5.7 (a) The D band peak position and (b) 2D band peak position of graphene with different hydrogen coverage as a function of excitation energy.

At low hydrogen coverage, both the electronic band structure and phonon dispersion of hydrogenated graphene are supposed to be similar to those of pristine graphene. However the red-shift of D and 2D band and the change in 2D band peak energy dispersion rate with increasing hydrogen coverage imply that both the electronic band structures and the phonon dispersion should be modified at medium hydrogen coverage (stage II and III), since the dispersion of D and 2D bands with laser energy is proportional to $v_{\text{Ph}}/v_{\text{F}}$, where v_{Ph} is the slope of the transversal optical phonon branch going through K point and v_{F} is the Fermi velocity, i.e. slope of the π band energy dispersion near K point [138]. Since a recent STM/STS measurement of defective graphene demonstrated the significant reduction in the Fermi velocity, the v_{Ph} should also

decrease with increasing hydrogen coverage [135]. At high hydrogen coverage, there might be a band gap at low energy level near the K point as predicted by theoretical calculation [121, 122], therefore the up shift of the π electron band would cause the significant red-shift of D and 2D band for all the excitation energies. Actually, opening a band gap at high hydrogen coverage was indeed observed, which will be demonstrated in section 5.4.

5.3 Thickness dependent hydrogenation and dehydrogenation

5.3.1 Thickness dependent hydrogenation

During our experiments, we found that hydrogenation of bi-layer graphene was much more feasible than that of single layer graphene on SiO_2/Si substrate. In order to intensively study this phenomenon, graphene layers with various layer numbers (1, 2, 3, 4, 5 and few layers) simultaneously presented in a single graphene flake were prepared (the sample in Figure 5.1 is an example). The thickness of the graphene layers was identified using Raman and contrast spectrum technique [22]. The graphene layers were subjected to hydrogen plasma treatments and subsequent thermal heating under identical conditions so that hydrogenation and dehydrogenation as a function of the layer number can be compared directly.

Figure 5.8 (a) shows Raman spectra (all the Raman spectra in this section were recorded by 532 nm excitation) of one to four-layer graphene layers (i.e. 1LG, 2LG, 3LG, 4LG) on the SiO_2/Si substrate prior to the hydrogenation treatments. The increase in layer numbers leads to significant broadening of the FWHM and blue-shift of the 2D band and the intensity of G band increases almost linearly with the increasing number of graphene

layers. In Figure 5.9 (a), Raman images generated by extracting the G band integrated intensity show clear contrast of the graphene sheets with various layer numbers at five different locations of the SiO₂/Si substrate. With Raman spectra and contrast spectra characterization, these five regions are identified as 1LG, 2LG, 3LG, 4LG and few (<10)-layer graphene (FLG), which are marked accordingly in Figure 5.9 (a).

Figure 5.8 (a) Raman spectra of pristine 1LG, 2LG, 3LG, and 4LG; (b) Raman spectra of 1LG, 2LG, 3LG, and 4LG hydrogenated by 10 W, 1 Torr hydrogen plasma for 1 min; (c) Raman spectra of 1LG, 2LG, 3LG, and 4LG dehydrogenated by vacuum annealing.

Figure 5.8 (b) shows Raman spectra of graphene layers after hydrogen plasma treatment (10 W, 1 Torr, 1 min). The D band is very sharp with a full width at FWHM of around 22 cm^{-1} in 1LG, and become much stronger, indicating more defects, in the 2-4LG after the hydrogen plasma treatment. D' peak is rather weak in 1LG but strong in 2-4LG so that it merges into G band as a shoulder. Figure 5.9 (b) shows the Raman imaging generated from the integrated intensity of D band of the same area after hydrogenation. It is interesting to find that the hydrogen coverage on 2LG and 3LG is higher than that of 1LG and 4LG. Moreover, for the graphene of 4 and more than 4 layers, the D band absolute integrated intensity decreases with the increase of graphene thickness, but still much higher than that of 1LG.

In section 5.2.1, we have got the conclusion that hydrogenation of graphene directly immersed in H_2 plasma should be attributed to the contribution of energetic ions and assume that the hydrogenation only happens on the top side for all the graphene layers [139]. If the hydrogen coverage on graphene with different layers is the same under identical hydrogenation conditions, the I_D/I_G is expected to decrease with increasing layer numbers. Moreover, according to D band activation model the absolute integrated intensity should be the same, which is contrary to our above observation. Therefore, it is obvious that, under the same hydrogen plasma treatment, the hydrogen coverage on graphene with different layers are different and the hydrogen coverage on 2-4LG is much higher than that on 1LG, indicating thickness dependent hydrogenation. Note that, after vacuum annealing of the hydrogenated graphene at $500\text{ }^\circ\text{C}$ for 30~45 min, the Raman bands related to the defects (D, D', D+G) induced by hydrogenation can be eliminated for all the graphene layers, as shown in Figure 5.8 (c).

Figure 5.9 (a) G band intensity Raman image of the pristine graphene sheet; (b) D band intensity Raman image of the graphene sheet hydrogenated by 10 W, 1 Torr hydrogen plasma for 1 min.

5.3.2 The mechanism of hydrogenation on graphene

The hydrogenation behavior of graphene layers was also studied with H₂ diffusion plasma (30W, 1Torr, 1min), using a Cu plate with small holes (hole size, ~0.5 mm) placed 2 mm above the graphene samples, which was previous used in chapter 3 to eliminate ion bombardments for growth of SWNTs at low temperatures. The grounded Cu plate with small holes can block most of the hydrogen ions from hydrogen plasma, and then reduce the density of hydrogen ions in the covered region, resulting in a much slower hydrogenation rate of graphene layers. Figures 5.10 (a) and (b) present the G and D bands

intensity image of a graphene sheet that contains one to five layers of graphene with the number of layers marked in the corresponding regions. The Raman spectra taken from 1LG, 2LG, 3LG, 4LG, 5LG and FLG after hydrogenation are shown in Figure 5.10 (c). It is clearly shown that at this relatively mild hydrogenation condition, the D band intensity of hydrogenated 2LG is still the highest and the D band intensity decreases with increased graphene layers. There is no obvious D band in the Raman spectra of 1LG; however the D band in the Raman spectra of multi-layer graphene is obvious. The evolution of D band intensity with the number of graphene layers here reconfirms the phenomenon that the hydrogen coverage is different on the graphene with different layers.

This complex D band intensity evolution of the hydrogenated graphene layers with the number of layers is totally different from the monotonous intensity evolution of D band induced by atomic hydrogenation [11,140]. Under the same plasma environment, different hydrogen coverage should be caused by different hydrogenation barriers. The phenomenon that hydrogenation of 2LG and 3LG is more feasible than that of 1LG and 4LG on SiO₂/Si substrate, indicates there is a transition number of the graphene layers with the lowest hydrogenation barrier. This conclusion seems to differ from that reported in other literatures [11,140], in which hydrogenation is more feasible on 1LG than that on 2LG. This difference resulted from different hydrogenation conditions. The graphene samples in reference 11 were hydrogenated by hydrogen atoms generated from remote hydrogen plasma. Our graphene samples were directly exposed to hydrogen plasma and immersed in the ocean of hydrogen radicals and energetic hydrogen ions (mostly the H₃⁺), which can effectively come over hydrogenation barriers. On the contrary, the hydrogen atoms in reference 11 are not so energetic, and the hydrogenation was believed to be

facilitated by high activity of convex surface in rippled graphene.

Figure 5.10 (a) G band intensity Raman image of a pristine graphene sheet; (b) D band intensity Raman image of the graphene sheet hydrogenated by hydrogen diffusing plasma (30 W, 1 Torr, 1 min); (c) Raman spectra of the hydrogenated graphene layers as a function of layer numbers.

The DFT study shows that binding a *H* atom on top of a *C* atom will shift the *C* atom around 0.3 Å along *Z* direction, resulting in an energy barrier of 0.2 eV for

chemisorption of atomic H on graphite/multi-layer graphene [141]. It is hard for the inactive atomic H produced by the hydrogenation approaches in reference 11 to overcome this energy barrier. Thanks to the intrinsic rippled atomic structure of 1LG [20], small amount of C atoms on the convex surface can chemisorb the H atoms with very small or no barriers, as the lattice of these C atoms is already deformed in the direction that favors sp^3 bonding, which lowers the total energy [11]. However, further hydrogenation of C atoms in other parts of 1LG still need to overcome an energy barrier. Therefore, unlike the graphite surface, 1LG has an ununiform distribution of hydrogenation barriers.

The hydrogenation process of 1LG by inactive H atoms might be attributed to the preferential sticking mechanism, which was demonstrated in the hydrogenation process on graphite surface and recent DFT investigation in hydrogenation of graphene [142-144]. After the first H atom is chemisorbed by a C atom on the convex surface with a very small barrier, the adsorption barrier for subsequent H in the vicinity of the already adsorbed H atoms further reduces or even vanishes due to $H-H$ interaction [142-144], which will cause the H atoms stick on C atoms step by step to form the hydrogenated clusters surrounded by non-hydrogenated C atoms, namely ununiform hydrogenation of 1LG reported reference 11.

The hydrogenation rate of above approach is relatively slow, which is consistent with the observation in reference 11 that hydrogenation duration is typically 2 hours for reaching the saturation state with the intensity ratio of D and G band at around 1. For 2LG with less rippled atomic structure [20], the preferential sticking hydrogenation mechanism cannot populate substantial H atoms due to the lacking of “the first H atoms”

chemisorbed by C atoms on convex surface. The preferential sticking hydrogenation of graphene layers by atomic hydrogen shows clear dependence on chemical reactivity controlled by graphene thickness.

For ionic hydrogenation, the energetic species in hydrogen plasma can overcome any energy barrier for hydrogenation of graphene layers. It should be pointed out that, when taking account of the possible penetration of hexagonal carbon network of the top graphene layer for the H^+ in plasma, the thickness dependent hydrogenation still can not be well explained. For example, in this situation, the hydrogen coverage on 3LG should be higher than or equal to that on 2LG, which is contrary to the observation in Figure 5.10. We believe the thickness dependent hydrogenation should result from corresponding energy barriers [141]. Under the same hydrogenation condition, the different hydrogen coverage on 1LG and 2LG indicates the corresponding hydrogenation barriers differ from each other. According to their lower hydrogenation barriers, multi-layers graphene, particularly the 2LG and 3LG, can reach their saturated hydrogen coverage much faster than the 1LG. The origination of thickness dependent hydrogenation barriers need to be further studied by DFT calculation.

5.3.3 Evaluation of hydrogen coverage on graphene layers

In order to verify above conclusions, hydrogen coverage on graphene layers were investigated using the scanning photoemission microscopy (SPEM) with a micro-focused beam [145]. The micro-SPEM was performed using the 8A1 beam line of the Pohang Accelerator Laboratory in Korea with incident photon energy of 630 eV and beam size of 1 μm . The C 1s core-level spectra were measured with an incident angle of 0° and an

emission angle of 55° , where the angle is 0° when the directions were perpendicular to the surface. A graphene sample with relatively large area, as displayed in Figure 5.11 (a), was employed for the micro-SPEM characterization. The graphene sample was exposed to 15 W, 1 Torr H_2 plasma for 1 min to get high hydrogen coverage. Figure 5.11 (b) and (c) show the Raman imaging and spectra of the graphene layers after hydrogenation. After micro-SPEM imaging of the hydrogenated graphene layers, XPS were extracted from desired regions.

Figure 5.11 (a) optical image of the graphene sample employed for SPEM, (b) D band intensity Raman image of the graphene sheet hydrogenated by H_2 plasma (15 W, 1 Torr, 1 min), (c) Raman spectra of the hydrogenated graphene layers.

Figure 5.12 C 1s core-level X-ray photoelectron spectra of 1LG, 3LG, and 5LG hydrogenated by 15 W, 1 Torr hydrogen plasma for 1 min.

The C 1s core-level spectra of hydrogenated 1LG, 3LG and 5LG are shown in Figure 5.12. The C 1s spectra can be fitted with three components. The main peak at a binding energy of 284.4 eV has been assigned to sp^2 hybridized C atoms in graphene [92]. Another peak at higher binding energy of 285.05 eV has been assigned to sp^3 hybridized C atoms due to the formation of C-H and C-C bonds by hydrogenation [92]. The other component located at lower binding energy at 283.5 eV is very weak, which may originate from the interface states and doping effect [146,147]. For 1LG, the intensity ratio of sp^3 and sp^2 hybridized carbon components is 0.2, corresponding to the hydrogen coverage of $0.2/1.2 = 16.67\%$, where 100% hydrogen coverage means every carbon atom in the top layer of graphene layers was hydrogenated [92]. At an excitation energy of $E_{hv} = 630$ eV, C1s photoelectrons have an $E_{kin} = 345$ eV and the corresponding attenuation length (λ) is about 8 Å [148]. With the electron escape depth of 4.6 Å ($d = \lambda \cos\theta$,

emission angle $\theta = 55^\circ$) and the graphene interlayer distance of 3.4 Å, we can roughly estimate that the signal from the top graphene layer contributes 60% and 55% for the sp^2 component intensity of 3LG and 5LG, respectively [148]. The intensity ratio of sp^3 and sp^2 hybridized carbon components of 3LG and 5LG are 0.5 and 0.3, respectively. Therefore, the hydrogen coverage of 3LG and 5LG are $0.5/(0.5+1 \times 0.6) = 45.5\%$ and $0.3/(0.3+1 \times 0.55) = 35.3\%$, respectively [92]. We noted that the hydrogen coverage of 3LG here is close to the saturation coverage on HOPG surface ($\sim 40\%$) [142,149]. The hydrogen coverage of 3LG is the largest among the three graphene layers we studied; the hydrogen coverage of 5LG decreased but still significantly higher than that of 1LG, which is constant with our observation by Raman imaging. The XPS characterization offers a strong support for above conclusion that the hydrogenation barriers of graphene layers show dependence on the layer number of graphene layers.

5.3.4 Thickness dependent dehydrogenation

Not only was the hydrogenation but also the dehydrogenation induced by thermal annealing found to be graphene thickness dependent. Moreover, interestingly, it was noticed that the dehydrogenation of graphene layers started at the temperatures as low as 75~100 °C. In order to study the dehydrogenation process in details, dehydrogenation monitored by Raman spectroscopy was performed in a thermal stage (Linkam TS1500) with the base vacuum pressure of 0.5 Pa. The single layer graphene (1LG) and bilayer graphene (2LG) with both low and high hydrogen coverage were employed for this experiment, for example, graphene layers hydrogenated with 5W and 15W, 1Torr H₂ plasma for 1 min. Figure 5.13 shows the Raman spectra of these samples. The samples

were rapidly heated (50 °C/min) to the desired annealing temperatures and then annealed for 30 min. Three Raman spectra were recorded for each step.

Figure 5.13 Raman spectra of 1LG and 2LG hydrogenated by 5 and 15 W, 1 Torr hydrogen plasma for 1 min.

After thermal annealing in vacuum, the Raman D band decreases in intensity relative to the G band. For graphene layers with low hydrogen coverages (samples hydrogenated by 5 W plasma), the I_D/I_G ratio (integrated intensity) starts to exhibit an obvious decrease with the annealing temperature as low as 75 °C, as shown in Figures 5.14 (a) and (c). Moreover, an interesting phenomenon is observed: when the samples were annealed with the increased temperature around 175-200 °C, the I_D/I_G ratio nearly remains unchanged, which means the residual defects cannot be thermally healed with the annealing temperature below 200 °C. With increasing annealing temperature, I_D/I_G ratio again starts to decrease rapidly and at last the D band vanishes completely. It seems

that there are two stages for the dehydrogenation process (I and II marked in Figure 5.14 (a) and (c)) with a boundary at around 175-200 °C, which should correspond to two types of dehydrogenation mechanisms with different dehydrogenation barriers, similar to the dehydrogenation process on graphite surface [149,150].

Figure 5.14 The evolution of the D and G band intensity ratio (I_D/I_G) with annealing temperatures in (a) 1LG and (c) 2LG hydrogenated by 5 and 15 W, 1 Torr H_2 plasma for 1 min; and the evolution of $\Delta(I_D/I_G)$ with annealing temperatures in hydrogenated (b) 1LG and (d) 2LG. The asterisk (*) denotes the as-treated sample by H_2 plasma.

To further study of the above-mentioned phenomenon, $\Delta(I_D/I_G)$, the difference in I_D/I_G at two adjacent annealing temperatures, was plotted with the annealing temperature

in Figure 5.14 (b) and (d). The fitting curves appear similar to the thermal desorption spectra of hydrogen on graphite surface [149]. In fact, with the hypothesis that the D band integrated intensity of the graphene layers within medium hydrogen coverage is proportional to hydrogen coverage, the Figure 5.14 (b) and (d) should be similar as the thermal desorption spectra with very low heating rate (50 K/1800 s). The thermal desorption spectra of hydrogen on graphite surface was interpreted with first order rate law, in which the dehydrogenation barriers show direct proportion to the desorption peak of annealing temperatures [149]. If the dehydrogenation of graphene also follows the first order rate law, the temperature peak in Figure 5.14 (b) and (d) can be used to roughly estimate the dehydrogenation barriers. As shown in Figure 5.14 (b) and (d), the desorption peak, i.e. the dehydrogenation barrier, of the dehydrogenation process I increase with increased hydrogen coverage, which should be attributed to the *H-H* interaction at higher hydrogen coverage [149,150]. The dehydrogenation barrier of 2LG in dehydrogenation process II is close to that of hydrogenated graphite surface [139,140], and larger than that of 1LG. This is consistent with recent DFT calculation that for single side hydrogenation, the hydrogenated 2LG has more stable structure than that of 1LG [121]. It should be point out that, for the highly hydrogenated graphene layers with high hydrogen coverage, such as 2LG hydrogenated by 15 W plasma, the hydrogen can also be totally healed by thermal annealing.

The recovery of graphene with high hydrogen coverage (hydrogenated by 15 W, 1 Torr H₂ plasma for 1 min) after thermal annealing was also recorded by the evolution of FWHM of D, G and 2D bands. The FWHM of G and 2D bands can slowly restore to their pristine state, as shown in Figure 5.15. For 1LG sample, the FWHM of G, D and 2D

bands decrease apparently at low annealing temperature (≤ 100 °C). For 2LG sample, FWHM of D and 2D bands keep unchanged at low annealing temperature (≤ 100 °C), and start to decrease at stage II (annealing temperature larger than 200°C). However the FWHM of G band reduces obviously even at low annealing temperature (stage I), suggesting that the dehydrogenation on 2LG with high hydrogen coverage can also happens at low annealing temperature. This dehydrogenation process can not be revealed by the changes in I_D/I_G ratio, because I_D/I_G is not proportional to the defect density in 2LG at high hydrogen coverage.

Figure 5.15 The evolution of FWHM of D, G and 2D bands with annealing temperatures in (a) 1LG and (b) 2LG hydrogenated 15 W, 1 Torr H_2 plasma for 1 min.

5.4 Electronic Structures of hydrogenated CVD graphene

5.4.1 Hydrogenation of as-grown CVD graphene on Cu foils

In order to investigate the efficiency of hydrogenation in tuning the electronic structures of graphene by spectroscopy characterization, the as-grown CVD single layer graphene on Cu foils were directly exposed to H_2 plasma for hydrogenation. After single

side hydrogenation, the Cu foils were etched by 0.2 M $\text{Fe}(\text{NO}_3)_3$ aqueous solution and graphene films were transferred onto SiO_2/Si and quartz substrates. It was noted that the hydrogenation of graphene on Cu foils required stronger plasma and longer duration than graphene on insulating substrates (SiO_2), as demonstrated by the Raman spectrum in Figure 5.16. For example, after hydrogenation with 10W 1 Torr H_2 plasma for 10 min, the graphene on SiO_2/Si substrates prepared by mechanical cleavage method (MCG) got high hydrogen coverage, which was reported in section 5.2, while such plasma dose produced quite low hydrogen coverage ($I_D/I_G = 1.25$) on CVD graphene/Cu samples.

Figure 5.16 Raman spectra of CVD single layer graphene hydrogenated by 10 W, 15 W and 20 W, 1 Torr H_2 plasma for 10 min, and Raman spectra of single layer graphene (mechanically cleaved on SiO_2/Si substrates) hydrogenated by 10W, 1 Torr H_2 plasma for 11 min.

When an insulating surface is immersed in plasma, a phenomenon known as

plasma-induced surface charging occurs in the presence of an electric field of plasma sheath [44]. The insulating surface accumulates net negative charges quickly and repelled the electron flux. In a steady-state plasma, the potential of the insulating surface (V_f) coupled to the plasma potential (V_p) via the sheath: $V_{sh} = V_p - V_f$, where V_p and V_{sh} is the potential of the plasma and plasma sheath respectively [44]. The V_p is always positive, and the V_f is negative [44]. On the other hand, when a conductive substrate is placed on the grounded anode, the V_f is 0 and therefore the potential of plasma sheath is significantly reduced, as illustrated in Figure 5.17, which will result in alleviated ion bombardments and weakened hydrogenation. This surface charging effect should be responsible for our observation.

Figure 5.17 Schematic diagram of the time average potential distribution between the upper electrode and grounded electrode in capacitively coupled radio frequency plasma.

5.4.2 Evaluation of hydrogen coverage

Figure 5.18 (a) shows the Raman spectra of pristine CVD graphene and CVD graphene treated with different plasma doses. The evolution of I_D/I_G and I_{2D}/I_G with increasing hydrogen coverage (or hydrogen plasma treatment dose) was plotted in Figure

5.18 (b). The I_D/I_G firstly increases with increasing hydrogen coverage as expected; however, at higher hydrogen coverage, it becomes saturated with a saturation value of 4.3, and subsequently decreases gradually. Differently, the I_{2D}/I_G exhibits a monotonic reduction with a relatively rapid trend. Such a decrease of I_D/I_G upon a critical amount of hydrogen coverage was previously studied in section 5.2 and interpreted based on a local activation model of Raman D band. Base on the study in section 5.2, we marked low and high hydrogen coverage region in Figure 5.18 (b).

Figure 5.18 (a) Raman spectra of pristine CVD graphene and hydrogenated CVD graphene with increasing hydrogen coverage. (b) The evolution of D/2D and G bands intensity ratio (I_D/I_G and I_{2D}/I_G) with increasing hydrogen coverage (hydrogenation dose).

The hydrogen coverage on graphene was further evaluated by XPS. XPS measurements were performed on ESCALAB 250 (Thermo VG Scientific) with monochromatic Al K α ($h\nu = 1486.6$ eV) as excitation. Figure 5.19 shows the C 1s core-level spectra of pristine CVD graphene and CVD graphene hydrogenated with different

Figure 5.19 *C 1s core-level X-ray photoelectron spectra of pristine CVD graphene and hydrogenated CVD graphene with increasing hydrogen coverage.*

H₂ plasma doses. The C 1s core-level spectra were fitted with two components: the main peak at a binding energy of 284.4 eV assigned to sp^2 hybridized C atoms in graphene, and another peak at higher binding energy of 285.1 eV assigned to sp^3 hybridized C atoms from C-H and C-C bonds formed by hydrogenation [92]. The hydrogen coverage was defined as $\theta/(1+\theta)$, where θ is the intensity ratio of sp^3 - and sp^2 -hybridized C components. The intensity ratio of sp^3 - and sp^2 -hybridized carbon components in the pristine CVD graphene is 0.1, corresponding to a value of $0.1/1.1 = 9.1\%$. The very weak sp^3 -hybridized carbon components in the pristine CVD graphene may originate from the absorption or trapping of CH₄ during CVD process. The C-H bonds are unlikely to be formed on pristine CVD graphene because there is no strong D band in the Raman spectrum. As indicated in Figure 5.19, the hydrogen coverages of hydrogenated

graphenes with increasing plasma treatment dose are 18%, 27% and 32%, respectively. As the XPS characterization was carried out *ex situ*, the hydrogen coverage of graphene cannot be evaluated accurately. The maximum hydrogen coverage (32%) obtained in our hydrogenation process is larger than the saturation coverage (25%) of single side hydrogenation proposed in the theoretical calculation [151].

5.4.3 Ultraviolet photoelectron spectroscopy characterization

The chemical bonding of H to an sp^2 -bonded C atom in the hexagonal lattice requires a local rehybridization from sp^2 to sp^3 , therefore hydrogenation are expected to show strong influence on the delocalized π electron system of graphene. As shown in Figure 5.20, valence-band spectra of pristine and hydrogenated CVD graphene obtained from photoelectron spectroscopy using He II radiation (40.8 eV) exhibit significant changes in π electron states below the Fermi level after being normalized to possess the same integrated intensity with respect to 0~15 eV binding energies. The spectrum of pristine CVD graphene excited by He II shows five band features, which are assigned as follows: (1) the band between 0 and 4 eV is associated with C 2p π electrons, in which the binding energy peak located at 3.2 eV corresponds to the 2p π electrons at Γ point, while the states between 0 and 2 eV corresponds to the 2p π electrons near the K point; (2) the binding energy peak located at 6 eV is resulted from the crossing of C 2p π and C 2p σ bands; (3) the binding energy peak located at 7.9 eV corresponds to C 2p σ electrons; (4) the binding energy peak located at 10.5 eV is the indication of the C s-p hybridized state; and (5) the band at ~13.5 eV represents C 2s σ electrons [93].

Figure 5.20 Relative variation of He II UPS valence band spectra of pristine CVD graphene and hydrogenated CVD graphene with increasing hydrogen coverage.

After hydrogenation process with low hydrogen coverage, parts of the delocalized 2p π states are transformed to C-H states, which cause the depression of the 2p π state with increasing hydrogen coverage. Although there are significant reductions of the density of 2p π states near Fermi level, the whole valence-band spectra keep similarity to that of the graphitic system associated with only a few changes in the electron states located at high binding energies. However, at high hydrogen coverage, two new electron states located at binding energies of 1.8 eV and 3.4 eV appear after complete depression of 2p π state, associated with obvious changes in the electron states located at high binding energies. Such a valence-band spectrum with two peaks below Fermi level is consistent with the recent calculated DOS of hydrogenated graphene with high hydrogen

coverage on single side [121]. The origin of these two electron states should be the sp^2 C clusters encircled by the sp^3 C matrix at high hydrogen coverage. The electron states at 3.4 eV should result from the localized π resonance in six- sp^2 C-ring encircled by sp^3 C-H [152], which is the most stable configuration proposed for 25% hydrogen coverage on single side [12,151]. The electron state located at 1.8 eV may originate from C dimer states formed at even higher hydrogen coverage, analogous to graphitic C dimer states on the reconstructed diamond (111) or (100) surfaces [110].

5.4.4 UV-Vis-NIR absorption spectroscopy characterization

The electronic structure of hydrogenated graphene was further investigated with optical absorption spectra in UV-Vis-NIR range. As shown in Figure 5.21, a broad optical absorption band at 4.6 eV, closing to the π plasmon energy reported in recent energy loss spectrum studies [153,154], was observed in UV-Vis absorption spectra of both pristine and hydrogenated CVD graphene. The 4.6 eV absorption peak corresponds to collective excitations of π electrons due to the π - π^* interband transition between the flat $2p\pi$ band regions at the M point [83]. This peak significantly red-shifted from the theoretic value of absorption peak arising from interband transitions of graphene and shows an asymmetric feature, which is proposed to be attributed to excitonic effects in graphene [83]. With increasing hydrogen coverage, this absorption band shows a broadened feature and blue-shift to higher energy with depressed intensity.

The absorption of pristine graphene at low photon energies ($0.6 \text{ eV} < E < 2 \text{ eV}$) exhibits a nearly flat absorption spectrum with a “universal opacity” of $\pi\alpha \approx 2.3\%$ as that observed in suspend graphene [84]. The significant drop in the absorption spectrum of the

pristine CVD graphene at $E < 0.6$ eV, as shown in the inset of in Figure 5.21, could be attributed to the chemical doping induced during the chemical etching and transfer process [76,155]. After hydrogenation, the features of the absorption spectra in NIR range keep nearly unchanged at low hydrogen coverage; however at high hydrogen coverage, there seems a weak absorption edge at 0.6 eV. With further increase of hydrogen coverage, the absorption edge at 0.6 eV becomes much clearer, indicating a gap opening (~ 0.6 eV) in graphene's electronic band structures, which is consistent with the flat band below Fermi level observed in the valence-band spectrum of HG-40W 10 min.

Figure 5.21 Absorption (Vis-UV) of pristine CVD graphene and hydrogenated CVD graphene with increasing hydrogen coverage. The inset shows their NIR absorption.

The band gap opening in hydrogenated graphene with high hydrogen coverage

was previously predicted by DFT calculation [121,151]. With sufficient hydrogen chemisorbed on graphene, the atomic structure as well as the electron structures of hydrogenated graphene strongly deviates from that of pristine graphene, forming graphene derivatives as a new kind of carbon material. However, at low hydrogen coverage, with the sp^3 C-H embedded within a sp^2 C matrix, the chemisorbed H behaves as defect in graphene and the defect scattering might not be able to lead a significant change in the optical absorption.

5.5 Conclusion

(1) An ionic hydrogenation process via H_2 plasma was developed for hydrogenation of graphene. The hydrogen coverage can be modulated to saturation state by adjusting the parameters such as plasma power and process duration, and the hydrogenation of graphene layers is reversible.

(2) For ionic hydrogenation, the hydrogenation rate of graphene layers is controlled by the hydrogenation energy barriers, which show clear dependence on the number of layers. The Raman spectra and micro-XPS spectra investigation demonstrated that the hydrogenation of bilayer and multilayer graphene was much more feasible than that of single layer graphene on SiO_2/Si substrate.

(3) Dehydrogenation was monitored by I_D/I_G and FWHM of D, G and 2D bands in Raman spectrum with different annealing temperatures. It has been revealed that there are two types of dehydrogenation mechanisms with different dehydrogenation barriers, which show significant dependence on the layer number of graphene sheets and the amount of the hydrogen coverage.

- (4) By Raman spectroscopy study of hydrogenated single layer graphene with multiple excitations, an excitation energy dependent saturation effect on I_D/I_G was revealed. A D band active model with D band Raman relaxation length and photoexcited electron/hole wavelength as critical length scales was developed for interpretation of this phenomenon.
- (5) The unusual decrease of I_D/I_G in Raman spectroscopy with increasing amounts of chemisorped hydrogen is an indicator for the high hydrogen coverage on graphene. At high hydrogen coverage, the Raman spectroscopy investigation indicated that both the structure and electronic bands of hydrogenated graphene significantly deviated from those of graphitic system.
- (6) The evolution of electronic structures of graphene with different amounts of hydrogen coverage was investigated by XPS, UPS and UV-Vis-NIR absorption spectroscopy. At low hydrogen coverage, the sp^3 C-H embedded within a sp^2 C matrix serves as defects in graphene, which depresses the delocalized π electrons significantly but has little influence on the optical properties, such as optical absorption. At high hydrogen coverage, two localized π electron states originated from the sp^2 C clusters encircled by the sp^3 C-H matrix appear in valence bands, and an opening of a band gap has been observed.
- (7) Our intensive study of electronic structures and structural evolution in hydrogenated graphene would provide a useful guide for developing applications of hydrogenated graphene, as well as other kinds of graphene derivatives.

Chapter 6

Conclusion and Future Work

6.1 Conclusion

Large-scale synthesis and comprehensive characterization of low dimensional carbon materials, including SWNTs, C_n @SWNTs, single layer graphene, bilayer graphene, nitrogen doped single layer graphene, and hydrogenated graphene were conducted in this thesis.

Wafer-scale synthesis of vertically aligned SWNTs by PECVD was achieved at low temperature (500 °C) with alleviated ion bombardments. The ion bombardment etching effect and selective etching effect in PECVD process had been intensively studied. For ion bombardment etching effect, the ion flux in discharge sheath, but not the ion bombardment energy, should be responsible. Both the aggressive ion bombardment and large C_2H_4/H_2 flow rate ratio can lead a structural transition from SWNT to few-walled nanotubes.

With low density plasma and special Co-Fe catalyst, linear carbon chains encapsulated in SWNTs, C_n @SWNTs, had been synthesized for the first time. The sizes of the linear carbon chains are around 1~2 nm and their HOMO-LUMO gaps is in near infrared range, which results in resonant Raman L bands with the 785 nm (1.58 eV) laser excitation. Carriers transport characterization indicates C_n @SWNT is an one dimensional metal with Luttinger-liquid behavior.

Single layer graphene and bilayer graphene can be synthesized homogeneously on

Cu foils in a controllable manner by low pressure CVD. The growth mechanism of bilayer graphene was found to be related to purity controlled catalytic activity of Cu surface. Both the electronic structure characterization and carrier dynamics study imply that the stacking order in bilayer graphene is close to AB staking and the electronic bands near K point are in split form.

Nitrogen-doped single layer graphene incorporated with N percentage up to 16% had been synthesized in presence of NH_3 . The structural and chemical imaging of nitrogen-doped single layer graphene showed that the distribution of incorporated N in graphene was in domains with size of 1~2 μm . The electronic structure characterization revealed that the N-C bonding configuration was pure pyridinic N. The pyridinic N efficiently changed the valence band structure of graphene, including the raising of density of π states near the Fermi level and the reduction of work function.

An ionic hydrogenation process via H_2 plasma was developed for hydrogenation of graphene. Both the hydrogenation and dehydrogenation of graphene layers show thickness dependent barriers. In Raman spectroscopy study of hydrogenated graphene, a excitation energy dependent saturation effect on the ratio of integrated intensities of D and G modes (I_D/I_G) was revealed and a D band Raman active model was developed for interpretation of this phenomenon. The evolution of structures and electronic structures of graphene with different amounts of hydrogen coverage was investigated. At low hydrogen coverage, sp^3 C-H embedded within a sp^2 C matrix serves as defects in graphene, which depresses the delocalized π electrons. At high hydrogen coverage, two localized π electron states originated from the sp^2 C clusters encircled by sp^3 C-H matrix appear in valence bands, and an opening of a band gap has been observed.

6.2 Future work

C_n @SWNTs is a unique one dimensional hybrid system. More intensive investigation of Raman spectroscopy and transport properties should be performed on an individual C_n @SWNT. Furthermore, the carrier dynamics and charge transfer in C_n @SWNTs probed by femtosecond pump-probe spectroscopy at varying temperatures should be an interesting topic.

The synthesis mechanism for AB stacked and misorientated bilayer graphene should be intensively investigated by studying of the growth dynamics on Cu foils with different purities. Regarding the characterization work, the study of electronic structures and carrier dynamics should be performed on both the pristine single layer/bilayer graphene and the intercalated/surface modified single layer/bilayer graphene [156].

Nitrogen doping in graphene has yet to be developed fully in a controllable manner. It is worthy to explore the dependence of electronic structures on the growth conditions, such as growth temperature, carbon sources ($C_2H_2/C_2H_4/CH_4$), nitrogen-containing precursors, flow rate ratios and even the Cu foils with different purities.

Our intensive study on hydrogenated graphene is a case study of graphene derivatives. Other decoration agent, such as F, O and metal atoms, should be interesting candidates. Further effort should be conducted on both the characterization of electronic structures and the device application of these graphene derivatives.

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