

# **Raman Imaging and Spectroscopy of Individual Single-Wall Carbon Nanotubes**

**By**

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## Approval Page

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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## **Abstract**

### **Raman imaging and spectroscopy of individual single-wall carbon nanotubes**

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Single-wall carbon nanotubes (SWNT) are unique one-dimensional materials that are promising for many potential applications in various important areas. Their vibrational properties reflect the electron and phonon confinement as well as the structures of the tubes. Resonant Raman spectroscopy has been proven to be an exceedingly powerful tool for the characterization of the vibrational and electronic properties of SWNTs. This thesis focuses on the study of Raman spectroscopy of individual single carbon nanotubes. Single tube spectroscopy allows probing the structure dependent properties of SWNTs.

A beam-scanning confocal Raman microscope system capable of large-area Raman imaging is first developed for characterizing SWNTs at the single tube level. Raman images and first-order Raman spectra of nanotubes, consisting of both semiconducting and metallic nanotubes, are systemically studied at room temperature in ambient air. The diameter of the nanotubes is determined from their radial breathing mode (RBM) frequency. A broad diameter distribution is observed for nanotubes synthesized by chemical vapor deposition. The tangential G mode Raman spectra of individual metallic nanotubes are found to exhibit a broad distribution of line shapes, which is attributed to shift of the Fermi level due to O<sub>2</sub> adsorption. The doping dependence of Raman spectra of metallic tubes is further studied by both

electrostatic gating and electrochemical gating. Significant changes in the G band Raman spectra of nanotubes are observed, suggesting the effect of doping on electron-phonon interaction. The observation of a gradual evolution of G band spectrum from a semiconducting type to the broad BWF type reveals evidence of phonon interaction between two G band modes.

Raman imaging and Raman spectra of isolated SWNTs and single-layer graphenene are investigated at both room temperature and low temperature. The temperature-induced Raman spectral change of individual nanotubes is observed to be tube diameter dependent, which can be ascribed to the temperature dependence of carbon-carbon bond force constant in SWNTs and the nanotube curvature effect.

At last, second-order Raman modes between  $1650$  and  $2000\text{ cm}^{-1}$  of small-diameter SWNTs are characterized under different excitation wavelength. Excitation wavelength dependent Raman spectra of the same nanotube reveals that frequencies of the overtone M band and combination iTOLA mode of a single tube are insensitive to excitation energy, which is in contrast to the dispersive behavior observed in the ensemble measurement. It is also discovered that the relative intensity of these second-order modes depends on the chirality and family type of a nanotube.

To my family

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## Chapter 1

### Introduction

Since carbon nanotubes were discovered by Ijima in 1991<sup>2</sup> and their single-wall form was discovered in 1993<sup>3</sup>, they have attracted tremendous interest from scientists in the past decade years. The reason that nanotubes are so attractive to scientists is because of their fascinating physical properties, which make them a model system for one-dimensional physics and may have large potential for applications. Single-wall carbon nanotubes (SWNTs), which are one atom in thickness, a few tens of atoms in circumference and hundreds of nanometers to exceeding 1 mm in length,<sup>4,5</sup> can be either metallic or semiconducting, depending on their diameter and chirality.<sup>6,7</sup> SWNTs have many potential applications including field-effect transistors,<sup>8-10</sup> light-emitting diodes,<sup>10-12</sup> sensors,<sup>13-17</sup> and biological imaging agents.<sup>18-24</sup>

The structure-dependent variation of the electronic properties of SWNTs can be advantageous for their promising applications. However at same time, it poses a significant challenge for the characterization of SWNTs, since the current synthesis methods lack control over the physical structures of the nanotubes produced. Bulk SWNT samples always consist of a mixture of nanotubes with different diameters and electronic properties. Single nanotube characterization is therefore important in understanding the structure-dependent properties of nanotubes and in developing nano-devices consisting of individual nanotubes.

Recent progress in catalytic chemical vapor deposition (CVD) synthesis enables the growth of ultra-long and oriented arrays of individual nanotubes on various substrates.<sup>4,5,25-27</sup> Individual ultra-long tubes and their oriented arrays not only

provide a desirable sample for single nanotube characterization but also generate many new applications that cannot be achieved with short or random network of nanotubes.<sup>28-30</sup> Single nanotube Raman imaging and spectroscopy, a fast and effective method for characterizing the as-grown individual nanotubes regarding their physical structure, diameter distribution, and relative populations of semiconducting and metallic nanotubes, may provide clues to SWNTs growth mechanisms and for controlling their uniformity.

In order to characterize SWNTs at the single tube level, it is necessary to identify and follow individual nanotubes precisely. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) have both been routinely used to image nanotubes, however only very limited structural information can be obtained from these two imaging methods. SEM cannot give precise structural determination of individual nanotubes on Si/SiO<sub>2</sub> wafers due to the charging effect.<sup>31</sup> It is also difficult to map individual tubes on a large-area sample by AFM, yet nanotube based devices often carry such geometries.

Resonance Raman spectroscopy (RRS) has been shown to be a powerful tool in the study of the electronic, vibrational, and structural properties of SWNTs.<sup>1,32-35</sup> Single-tube Raman spectroscopy, enabled by the strong resonance enhancement effect associated with the exciton transition,<sup>36-38</sup> has become an important nondestructive characterization tool to study the structure-dependent properties of ultra-long nanotubes on a substrate<sup>38-40</sup> and even nanotubes underneath a dielectric layer.<sup>41</sup>

The work in this thesis involves the study of first-order and second-order Raman spectroscopy of individual SWNTs in various conditions<sup>42-45</sup> by using a laboratory-designed laser scanning confocal microscope system.<sup>46</sup> The organization of this thesis is as follows:

In chapter 2, the structures and growth methods of single-wall carbon nanotubes are presented first. Then, an introduction to the electronic structures of SWNTs is given, followed by a general introduction of Raman scattering process.

Chapter 3 focuses on the experimental equipments and procedures used in the work.

Chapter 4 presents the general observation of Raman imaging and first-order Raman spectra of individual SWNTs, and the structural assignment of SWNTs based on Raman spectroscopy.

Chapter 5 contains work on charge doping dependence of G band Raman spectra of metallic nanotubes by both electrostatic and electrochemical gating. The result suggests strong electron-phonon interaction as well as evidence of LO-TO phonon interaction.

Chapter 6 describes the temperature-dependence studies of RBM and G band Raman spectra of semiconducting and metallic tubes. The data show a diameter dependence of the temperature-induced spectral changes.

Chapter 7 focuses on the second-order Raman spectra of isolated small-diameter SWNTs. The M band, RBM+G combination mode, and iTOLA combination mode are characterized under different excitation wavelength.

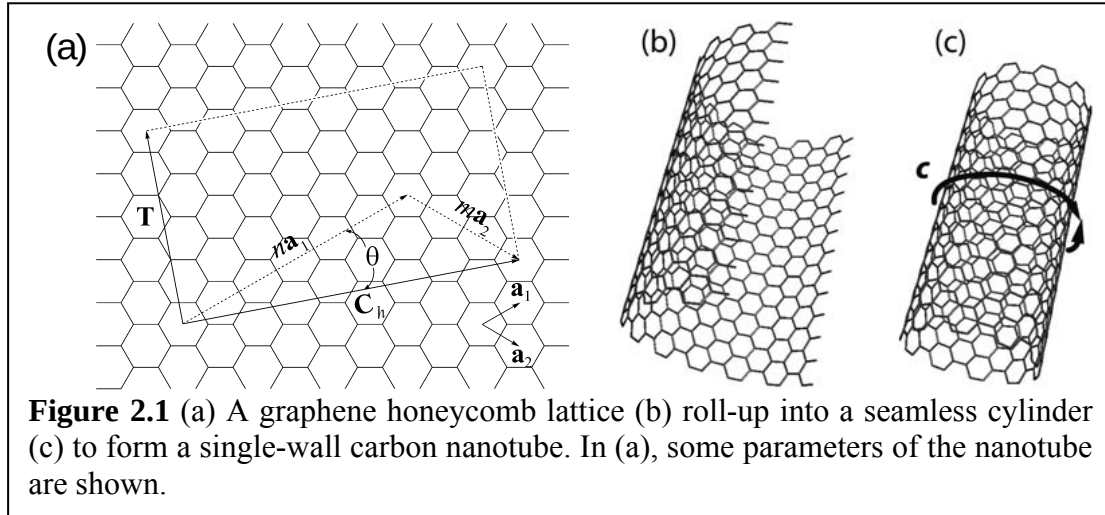
Finally, a summary is given in Chapter 8.

## Chapter 2

### Background

#### 2.1. Structure and parameters

A Single-wall carbon nanotube (SWNT) can be viewed as a single-layer graphene sheet rolled up into a seamless cylinder, as shown in Figure 2.1. Normally SWNTs are one atom in thickness, a few nanometers in diameter and up to micrometer in length. Figure 2.1a shows the graphene honeycomb lattice. Since the microscopic structure of carbon nanotubes is derived from that of graphene, the tubes are usually labeled in terms of the graphene lattice vectors, as shown below.



For each SWNT, the specific vector which spans the circumference is the so-called chiral vector or roll-up vector  $\mathbf{C}_h$ :

$$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 .$$

Here  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the two unit vectors in the graphene lattice, as shown in Figure 2.1a. The integers  $n$  and  $m$  ( $n \geq m$ ) denote the numbers of unit vectors along hexagonal honeycomb lattice in the chiral vector.  $(n, m)$  are also called the chiral index, which describe the unique structure of each SWNT and hence determine all other structural parameters.

The diameter of a  $(n, m)$  nanotube can be obtained from the chiral vector by

$$d_t = \frac{C_h}{\pi} = \frac{\sqrt{3}a_{C-C}(m^2 + mn + n^2)^{1/2}}{\pi},$$

where  $a_{C-C}$  is the adjacent C–C distance and  $C_h$  is the length of the chiral vector  $\mathbf{C}_h$ .

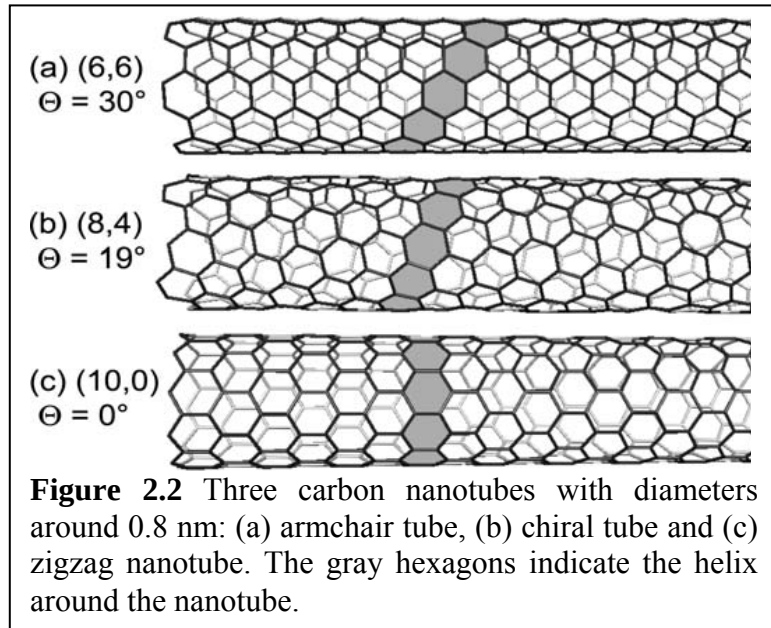
For tubes with similar tube diameter, their structures will be various.

Another important parameter is the so-called chiral angle  $\theta$  which is the angle between the chiral vector and the direction of the unit vector  $\mathbf{a}_1$ . It is also determined by the chiral vector and can be written in terms of the chiral indices  $(n, m)$  as

$$\theta = \tan^{-1} \left[ \frac{\sqrt{3}m}{m + 2n} \right].$$

The chiral angle is allowed to vary between  $0^\circ$  and  $30^\circ$ . Other range ( $30^\circ$  to  $360^\circ$ ) can

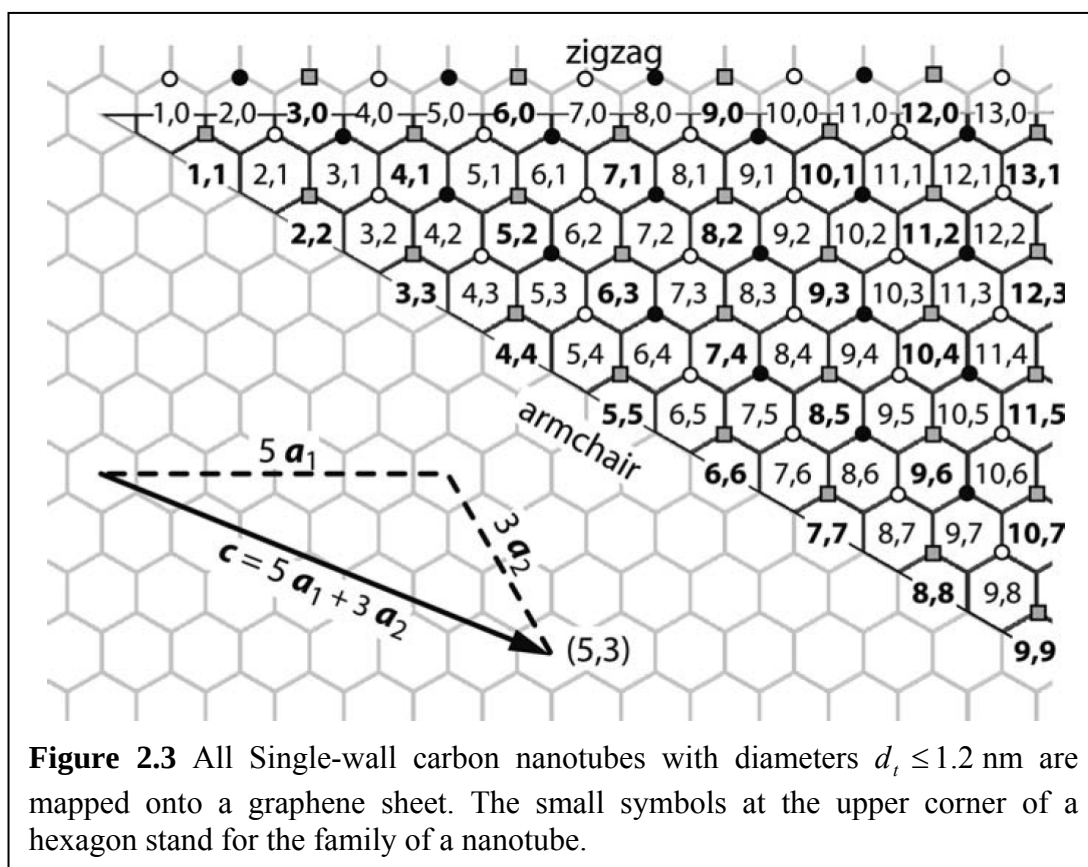
be converted to this range due to the hexagonal symmetry of graphene. Figure 2.2 shows three nanotubes with different chiral angle but similar diameters around 0.8 nm.<sup>47</sup> The nanotube



with the chiral angle  $\theta = 0^\circ$  is the so-called *zigzag* nanotube, whose name derives from the zigzag chain forming the edge of this high-symmetry type of tube, as in Figure 2.2c. On the other hand, the tube with  $\theta = 30^\circ$  is called *armchair* nanotube, whose edge resembles a row of armchairs when viewed from above (Figure 2.2a). The general nanotubes with chiral angle  $0^\circ < \theta < 30^\circ$  are referred to as chiral nanotubes, whereas zigzag and armchair tubes are both called achiral tubes since they

have a particular higher symmetry. Achiral tubes have several properties that distinguish them from chiral tubes. For example, armchair nanotubes are the only tubes whose electronic band gap is strictly zero.

We also can use a very useful illustration which draws all possible nanotubes of a given diameter range on a graphene lattice, as in Figure 2.3, to describe achiral



and chiral tubes.<sup>47</sup> In the illustration, the tubes along the horizontal edge are zigzag tubes, while those running along  $30^\circ$  direction away from horizontal direction are armchair. From this illustration, we can easily study systematic properties of nanotubes, such as their metallic and semiconducting character, the family behavior, and nanotube branches. These topics will be introduced in later chapters.

Depending on their chirality, SWNTs can be metallic or semiconducting. In general, SWNTs can be sorted into three families, according to whether  $\text{MOD}(2n + m, 3) = 0, 1, 2$ , where the integers are the remainders of division of  $(2n + m)$  by 3. Back to Figure 2.3, the small symbol at the upper corner of a hexagon indicates the

family type of a nanotube: closed circles refer to MOD1 family; open circles refer to MOD2 family; squares refer to MOD0 family. From the illustration, we note that the tubes from the same family are connected by armchair-like directions. Among the three families, MOD1 and MOD2 are the two semiconducting nanotube families, while MOD0 is the metallic or quasi-metallic family. From Figure 2.3 we see that every metallic tube (squares) is surrounded by six semiconducting neighbors (open and closed circles).

Some important nanotubes' parameters, including those that have not been introduced so far, are summarized in Table I.

**Table I.** Parameters for carbon nanotubes

| Parameter                                      | Armchair ( $n, n$ )              | Zigzag ( $n, 0$ )              | Chiral ( $n, m$ )                                                     |
|------------------------------------------------|----------------------------------|--------------------------------|-----------------------------------------------------------------------|
| Length of unit vector $a_0$                    | $\sqrt{3}a_{CC}$                 |                                |                                                                       |
| Chiral vector $\mathbf{C}_h$                   | $n(\mathbf{a}_1 + \mathbf{a}_2)$ | $n\mathbf{a}_1$                | $n\mathbf{a}_1 + m\mathbf{a}_2$                                       |
| Diameter $d_t$                                 | $\sqrt{3}a_0 n / \pi$            | $a_0 n / \pi$                  | $a_0 \sqrt{n^2 + nm + m^2} / \pi$                                     |
| Chiral angle $\theta$                          | $30^\circ$                       | $0^\circ$                      | $\tan^{-1} \left[ \frac{\sqrt{3}m}{m + 2n} \right]$                   |
| Translational vector $\mathbf{T}$              | $\mathbf{a}_1 - \mathbf{a}_2$    | $\mathbf{a}_1 - 2\mathbf{a}_1$ | $\frac{2m + n}{d_R^*} \mathbf{a}_1 - \frac{2n + m}{d_R} \mathbf{a}_2$ |
| Point group                                    | $D_{2nh}$                        | $D_{2nh}$                      | $D_q$                                                                 |
| Number of hexagons in the nanotube unit cell N | $6n$                             | $2n^2$                         | $\frac{2(n^2 + m^2 + nm)}{d_R}$                                       |

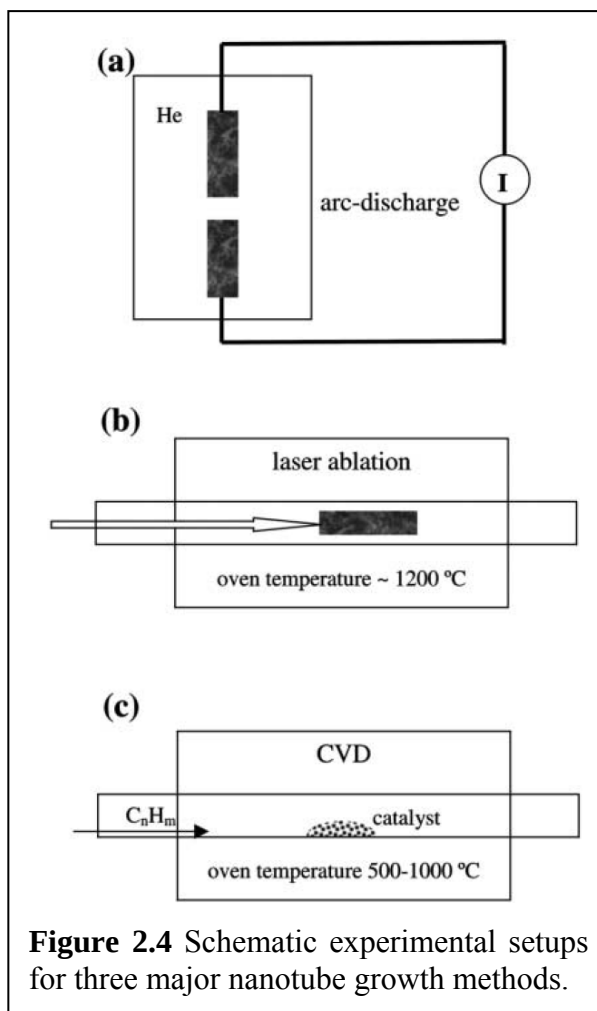
\*  $d_R$  is the greatest common divisor of  $(2n + m)$  and  $(2m + n)$

## 2.2. Growth and synthesis

In order to fully understand the characteristics and the potential of carbon nanotubes, well-controlled and optimized growth of nanotubes is necessary. In recent years, several growth methods have been well developed. However, many challenges still remain in this area. First, an efficient approach to grow structurally perfect nanotubes at large scales is still lacking. Second, growing defect-free nanotubes

continuously to macroscopic lengths has been difficult. Third, it is seemingly difficult to control the chirality of SWNTs during any existing growth method.

There are three major growth methods: laser ablation, arc-discharge, and chemical vapor deposition (CVD).<sup>2,3,48</sup> The schematic experimental setups for these three methods are shown in Figure 2.4.<sup>48</sup> All growth processes have the similarity that a carbon plasma is formed either by heating or by chemical decomposition. The tubes grow when metal catalysts are added to this plasma. The type of catalyst and the growth conditions can determine whether single, double or multi-wall tubes are grown. Besides the number of walls, the yield, tube diameter and length can be controlled during growth.



### 2.2.1. Arc-discharge and laser ablation

Arc-discharge and laser ablation are the first two processes that produced nanotubes with high yield.<sup>49,50</sup> Both methods involve evaporation of a solid carbon source to generate the condensation of carbon atoms. Therefore the temperatures in these methods are close to the melting temperature of graphite, 3000-4000°C.

In arc-discharge (Figure 2.4a), carbon atoms are evaporated by a plasma of helium gas ignited by high currents passed through opposing carbon anode and cathode. Arc-discharge is an excellent method for growing both high quality multi-wall nanotubes (MWNTs) and single-wall nanotubes. By controlling the growth conditions such as the pressure of inert gas in the discharge chamber and the arcing current, high quality MWNTs can be obtained at the gram level.<sup>51</sup> The length of the synthesized MWNTs can reach the order of ten microns and the diameter is in the range of 5-30 nm. However the nanotubes are typically bound together by strong van der Waals interactions and form tight bundles, which are difficult to separate. Also there are few defects such as pentagons or heptagons existing on the sidewalls of the tubes. During the arc-discharge growth process, by-products are mainly multi-layered graphitic particles in polyhedron shapes, which can be removed by heating the as grown material in an oxygen environment.<sup>51</sup>

In 1993, substantial amounts of SWNTs were successfully produced by arc-discharge. In contrast to MWNTs, a metal catalyst is necessary for the growth of SWNTs in an arc-discharge system. However, the growth of high quality SWNTs at the 1-10g scale was achieved by Smalley and coworkers by using a laser ablation method.<sup>49</sup> In the laser ablation method (Figure 2.4b), a pulsed laser is used to ablate a carbon target in a tube-furnace heated to high temperature while a flow of inert gas is bled into the chamber. Nanotubes develop on the cooler surfaces of the tube-furnace as the vaporized carbon condenses. The grown nanotubes are carried downstream by the flow of inert gas to be collected. The SWNTs produced by laser ablation are mostly in the form of bundles consisting of tens of individual tubes close-packed into hexagonal crystals via van der Waals interactions. For more than ten years it has been a great challenge to break these bundles and prevent the isolated tubes from

rebundling. This problem was solved in 2002 by a postprocessing routine, where first the bundles are broken apart by ultrasonification. The tubes are then coated by a surfactant to eliminate interactions between them. Finally, the remaining small bundles with 3-10 tubes are removed from the solution with a centrifuge. In this way, solutions with isolated nanotubes were produced for a wide range of nanotubes.

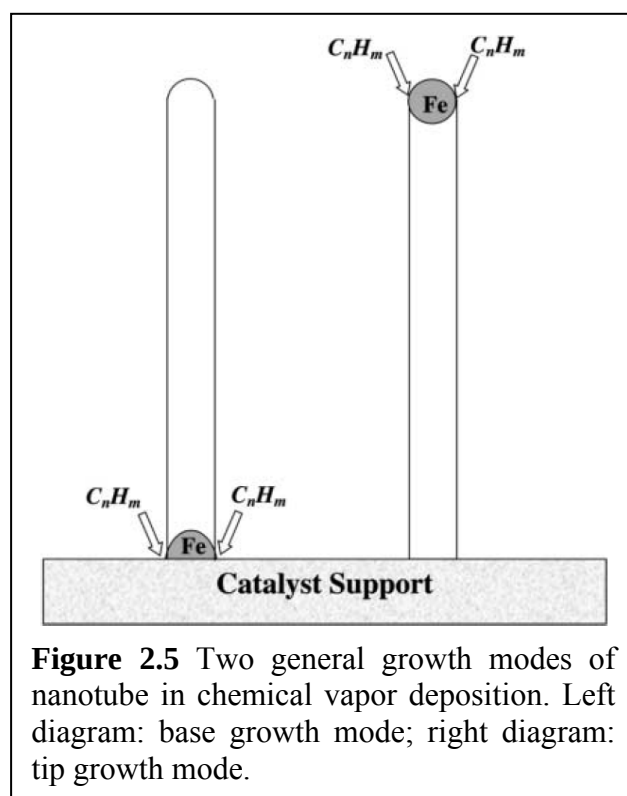
In SWNT growth by arc-discharge and laser ablation, typical by-products include fullerenes, graphitic polyhedrons with enclosed metal particles, and amorphous carbon in the form of particles or overcoating on the sidewalls of nanotubes. A purification process for SWNT materials, which was developed by Smalley and coworkers,<sup>52</sup> is widely used. The method involves refluxing the as-grown SWNTs in a nitric acid solution for an extended period of time, oxidizing away amorphous carbon species and removing some of the metal catalyst species.

### **2.2.2. Chemical vapor deposition**

Recently Chemical vapor deposition (CVD) has become the most widely used growth technique, since it is cheap, scalable and allows a high degree of control over the tubes. Compared with arc-discharge and laser ablation, CVD method has several advantages. First, with CVD it is possible to grow nanotubes on well-defined places with patterned substrates, for example to produce an individual tube that bridges two catalytic particles. Second, CVD growth can work at lower growth temperatures. As discussed above, Arc-discharge and laser ablation rely on evaporating carbon atoms from solid carbon sources at 3000-4000°C, which is not efficient and limits the scale-up of SWNTs. Whereas for CVD, the growth temperature could be less than 1000°C. Another very important advantage is that CVD tends to produce isolated nanotubes rather than bundled tubes, which is particularly important for optical studies and

Raman spectroscopy on single SWNTs. In contrast to bundled tubes, isolated nanotubes behave like truly one-dimensional systems from an optical point of view. They show sharp absorption peaks and Raman resonances. However there are also disadvantages in the CVD method. The great disadvantage of CVD is the lower quality of nanotubes obtained compared to that of tubes produced by the other two methods.

In the CVD method, a substrate is prepared with a layer of metal catalyst



particles, most commonly nickel, cobalt, iron, or a combination. Then it is placed in a tube furnace and is heated to high temperature. After that, a hydrocarbon gas flows through the tube reactor for a period of time for tube growth. The key parameters in CVD growth are the hydrocarbons, catalysts and growth temperature. The active catalytic species are typically

transition-metal nanoparticles formed on a support material such as alumina. The general nanotube growth mechanism (Figure 2.5<sup>48</sup>) in the CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, and dissolution and saturation of carbon atoms in the metal nanoparticle. The precipitation of carbon from the saturated metal particle leads to the formation of tubular carbon solids with  $sp^2$  structure. Tubule formation is favored over other forms of carbon such

as graphitic sheets with open edges since a tube contains no dangling bonds and has a lower energy than other forms.

For MWNT growth, most of the CVD methods employ ethylene or acetylene as the carbon feedstock and the growth temperature is typically in the range of 550-750°C. Iron, nickel or cobalt nanoparticles are often chosen as catalysts, since carbon has finite solubility in these metals, and it forms metal-carbon solution at high temperature. However, a major drawback for CVD grown MWNTs is that they have high defect densities in their structures. This is most likely due to the relatively low growth temperature, which does not provide sufficient thermal energy to anneal nanotubes into perfectly crystalline structures.

For a long time, perfect SWNT materials have been mainly produced by arc-discharge and laser ablation methods. Recently, CVD method is able to grow SWNTs with structural perfection. In CVD, the choice of carbon feedstock is one of the key elements to the growth of high quality SWNTs containing no defects and amorphous carbon over-coating. Among all hydrocarbon molecules, methane is found to be good carbon source since it is the most stable at high temperatures against self-decomposition. Also it was found that the chemical and textural properties of the catalyst materials dictate the yield and quality of SWNTs. A good catalyst material should exhibit strong metal-support interactions, possess a high surface area and large pore volume. Moreover, these textural characteristics should remain intact at high temperatures without being sintered.

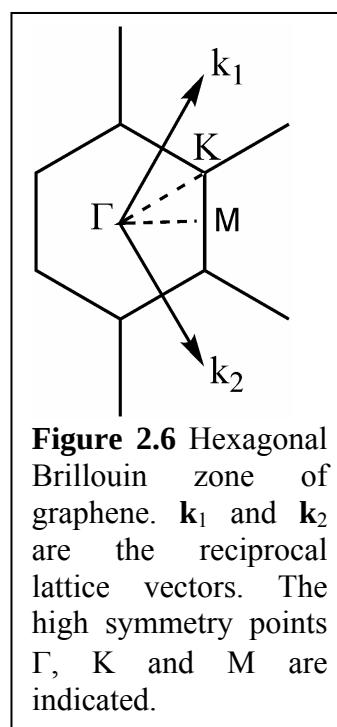
The growth of carbon nanotubes remains a rapidly evolving field. However there is still much work, especially on the theoretical side, that needs to be done for a better understanding of the growth process.

## 2.3. Electronic structure

Compared with its simple microscopic structure, the electronic structure of a carbon nanotube is much complex. For example, a (10, 5) and a (10, 6) tubes are almost indistinguishable concerning their atomic structures, but they have drastic differences in their electronic properties. This is one of the reasons why carbon nanotubes evolved into a model system for one-dimensional nanostructures. Since carbon nanotubes can be described as being derived from the 2D graphene sheet, the electronic structure of a carbon nanotube can be obtained from its parent material 2D graphite when only first order is considered. Therefore before understanding how the quantization condition can be used to estimate the electronic band structure of carbon nanotubes from the electronic states of graphene, the electronic structure of graphene will be briefly described.

### 2.3.1. Electronic structure of 2D graphene

Graphene is a semimetal, which means that its valence and conduction bands cross, but the electronic density of states is zero at the Fermi level (the crossing point). In the 2D graphene sheets, the electronic  $\sigma$  bands are responsible for the strong in-plane covalent bonds, while the  $\pi$  bands are responsible for weak van der Waals interactions between such graphene sheets in 3D graphite. In contrast to the  $\sigma$  bands, the  $\pi$  bands are close to the Fermi level, so that electrons can be excited from the valence ( $\pi$ ) to the conduction ( $\pi^*$ ) band optically. Therefore the most widely used description of the electronic band structure

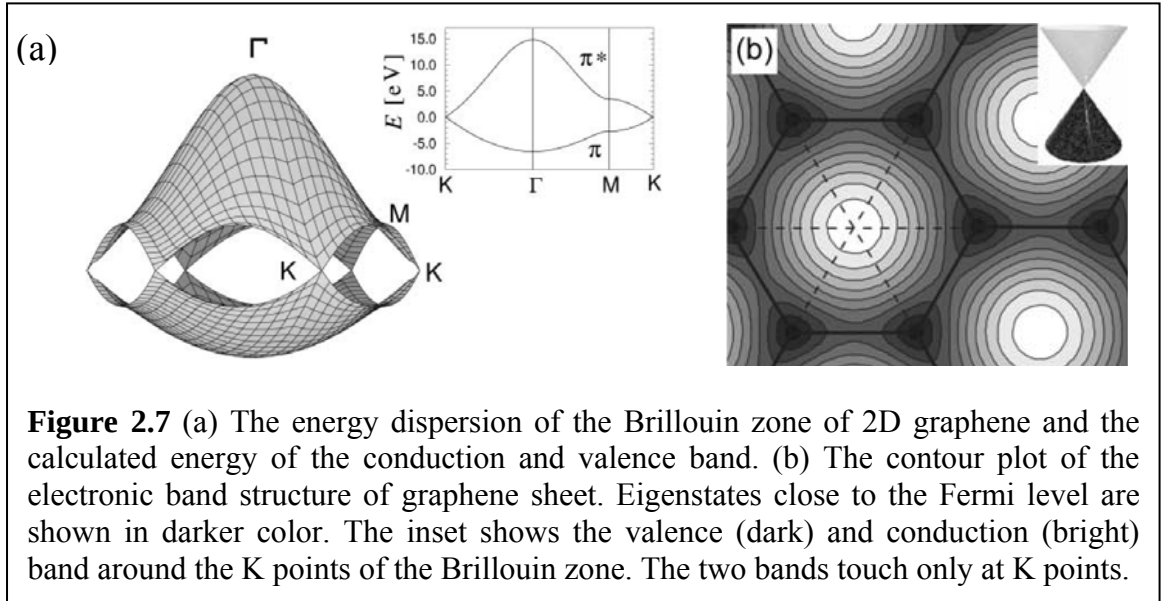


of graphene is an empirical tight-binding model, which includes only the  $\pi$  states perpendicular to the graphene sheet and their interactions. In this model, the interaction between the carbon electrons to nearest neighbors in the graphene sheet is restricted and the overlap between two  $\pi$  wave functions centered at different atoms is also neglected. Under these approximations the valence  $E^-$  and conduction bands  $E^+$  of graphene are given by the simple analytic expression<sup>47</sup>:

$$E^\pm(\mathbf{k}) = \gamma_0 \sqrt{3 + 2 \cos \mathbf{k} \cdot \mathbf{a}_1 + 2 \cos \mathbf{k} \cdot \mathbf{a}_2 + 2 \cos \mathbf{k} \cdot (\mathbf{a}_1 - \mathbf{a}_2)} .$$

Here  $\gamma_0$  describes the interactions between two  $\pi$  electrons.  $\mathbf{k}$  is the electronic wave vector for the graphene Brillouin zone (Figure 2.6) and  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the lattice vectors.

In Figure 2.7a, the electronic energy dispersion for 2D graphene as a function of the wave vector  $\mathbf{k}$  in the hexagonal Brillouin zone has been shown in two different forms.<sup>53</sup> From them, we can see that the valence ( $\pi$ ) and the conduction ( $\pi^*$ ) band touch each other only at K points. In this way, the Fermi energy corresponds to zero energy at K points. Figure 2.7b shows the corresponding equi-energy contour of the



electronic band structure of graphene.<sup>47</sup> Seen from the contour plot, the valence and

conduction bands near K points have a linear dependence on wave vector  $\mathbf{k}$ . The linear energy dispersion relations for conduction (+) and valence (-) band can be given by<sup>54</sup>

$$E^{\pm}(\mathbf{k}) = \pm \frac{3}{2} \gamma_0 \mathbf{k} a_{C-C}.$$

Therefore if only considering small  $\mathbf{k}$  vectors, it is very convenient to use the above function for interpreting the experiment results. The inset of Figure 2.7b shows the cones which represent the band structure very close to the Fermi level.

The nearest-neighbor tight-binding model is enough to describe well the electrons close to the Fermi energy. However, in the range of optical-transition energies, it has more deviation from ab-initio calculations and from measurement, which can be fixed by including more neighbors. For example, if up to third-neighbor interaction and the overlap between the  $\pi$  wave functions are included, there is virtually no difference between the semiempirical description and first-principles results.

### 2.3.2. Electronic band structure of SWNTs

As mentioned above, the electronic band structure of SWNTs can be obtained from that of graphene. However in the case of SWNTs, the quantum confinement of the 1D electronic states must be taken into account since SWNTs are one-dimensional solids. For an instant, along the nanotube circumference electrons, phonons and other quasiparticles can only have certain discrete wavelengths, because of the periodic boundary conditions. On the other hand, quasiparticles can travel along the nanotube axis. An infinitely long tube has continuous electronic and vibrational states in this direction. However, since the local crystal structure of the nanotubes is so close to that of a graphene sheet and the Brillouin zone is small, Brillouin zone-folding techniques

are still commonly used to obtain approximate electron and phonon dispersion relations for carbon nanotubes.

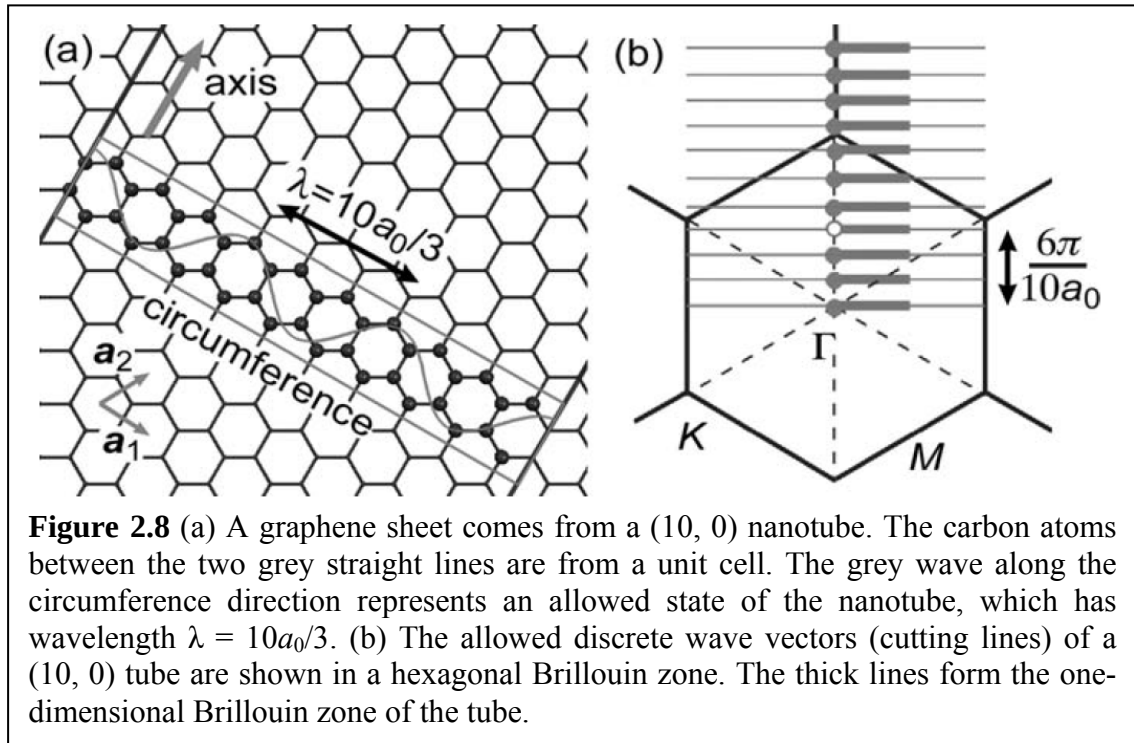
Due to the periodic boundary conditions in the circumferential direction, for carbon nanotubes, only a certain set of  $\mathbf{k}$  states is allowed. The allowed set of  $\mathbf{k}$  states, which are indicated as cutting lines in the hexagonal Brillouin zone, depends on the diameter and chirality of nanotubes. For a  $(n, m)$  tube, the discrete unit wave vector along the circumference direction is given by<sup>53</sup>

$$\mathbf{k}_\perp = \frac{2n+m}{Nd_R} \mathbf{k}_1 + \frac{2m+n}{Nd_R} \mathbf{k}_2,$$

while the reciprocal lattice vector along the nanotube axis direction is given by<sup>53</sup>

$$\mathbf{k}_z = \frac{m}{N} \mathbf{k}_1 - \frac{n}{N} \mathbf{k}_2.$$

Here  $d_R$  and  $N$  have already been given in table I, and  $\mathbf{k}_1$  and  $\mathbf{k}_2$  are the reciprocal lattice vectors of 2D graphene (see Figure 2.6). For each nanotube, there are  $N$  discrete  $\mathbf{k}$  vectors (cutting lines) in the circumferential direction, which can be indicated as  $\mu \mathbf{k}_\perp$  ( $\mu = 1 - N/2, \dots, N/2$ ). Figure 2.8a shows one allowed wave vector



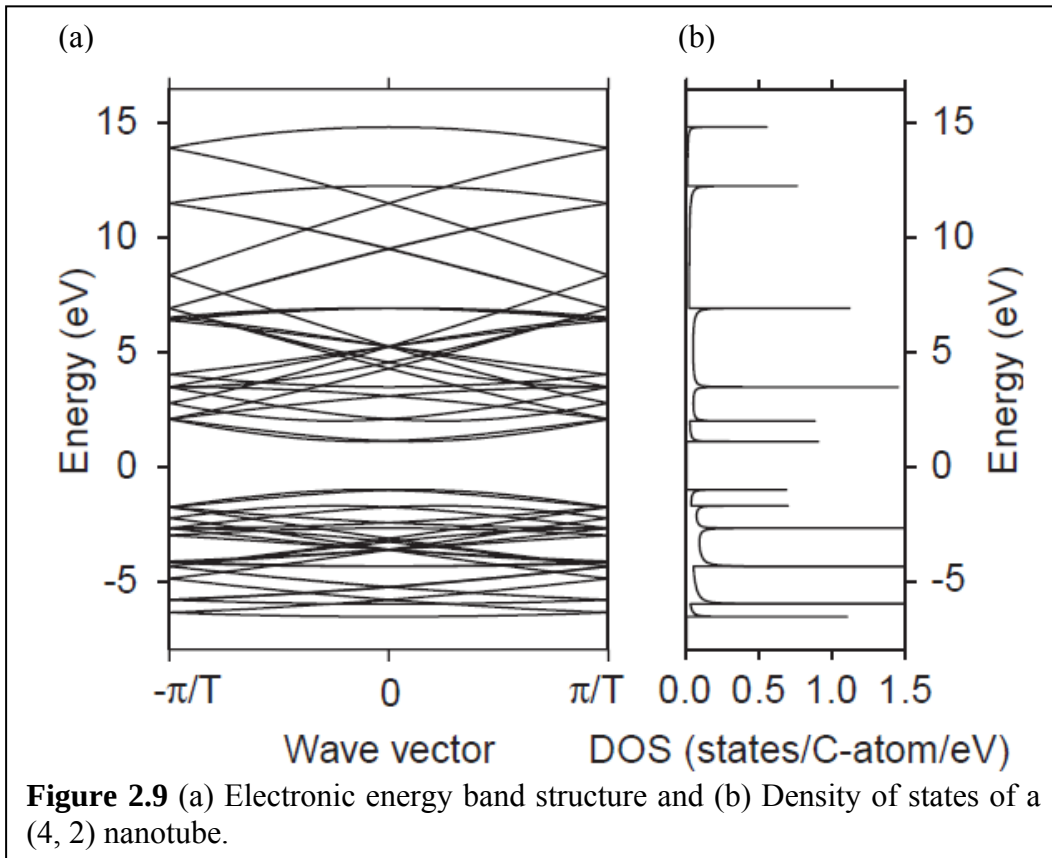
along circumference direction on a graphene sheet for a (10, 0) tube.<sup>53</sup> The wave has wavelength  $\lambda=10a_0/3$ . Figure 2.8b shows several cutting lines of same tube in the Brillouin zone.

The 1D energy dispersion relations of a SWNT, which can be obtained by zone-folding of the band structure of the 2D graphene sheet ( $E_g^\pm$ ), are given by<sup>55</sup>

$$E_\mu^\pm(\mathbf{k}) = E_g^\pm\left(\mathbf{k} \frac{\mathbf{k}_z}{|\mathbf{k}_z|} + \mu \mathbf{k}_\perp\right).$$

By translating the N pairs of energy dispersion curves given by the above equation to the first Brillouin zone of 2D graphene sheet, we can easily obtain the band structure of the nanotube, which is shown in Figure 2.9a. The 1D density of states (DOS) can be calculated by<sup>26</sup>

$$D(E) = \frac{T}{2\pi N} \sum_{\pm} \sum_{\mu=1}^N \int \frac{1}{\left| \frac{dE_\mu^\pm(\mathbf{k})}{d\mathbf{k}} \right|} \delta(E_\mu^\pm(\mathbf{k}) - E) d\mathbf{k}.$$



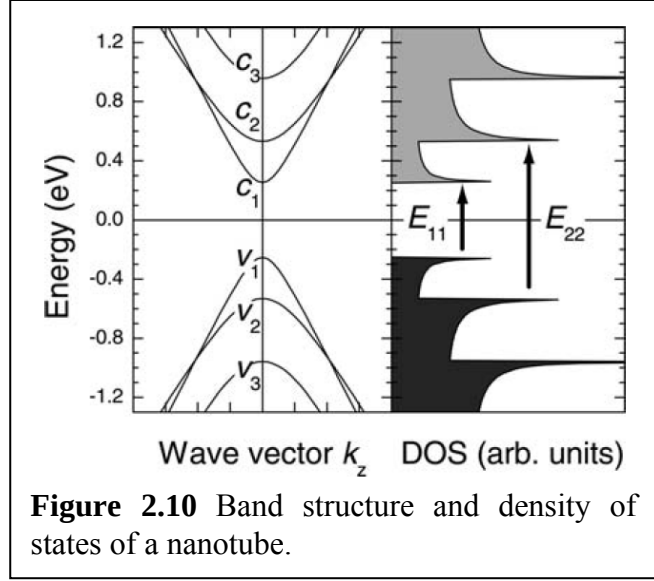
Compared with the 1D band structure, the 1D DOS (Figure 2.9b) appears much simpler. The van Hove singularities (vHSs) in the DOS, which is due to the one-dimensional property of nanotubes, are proportional to  $E_{\mu}^{\pm}$  at both energy minima and maxima of the dispersion relations. Since the cutting line direction, which is along the circumference, depends on the nanotube chiral angle, the energies where the vHSs arise have chirality dependence. Also the distance between two near-by cutting lines is equal to  $2/d_t$ , that brings the  $1/d_t$  dependence to the distance of vHSs. Because of these two dependences, each SWNT has a different set of vHSs in its valence and conduction bands. Therefore vHSs are very important to understand the solid states properties of nanotubes, for example the resonance Raman spectroscopy.

### 2.3.3. Band to band transition and Kataura plot

When an electron is excited from the valence into the conduction band, a band to band transition occurs. According to the optical selection rules for carbon nanotubes, the optical transitions only happen between electronic bands with same symmetry ( $\Delta i = 0$ ) for z polarization light (along the nanotube axis). For perpendicular polarization light, the allowed symmetry is  $\Delta i = \pm 1$ . However in this case, the optical transition is strongly suppressed by the anisotropic polarizability. Thus in nanotube case, we only consider the optical transitions with  $\Delta i = 0$ .<sup>5</sup>

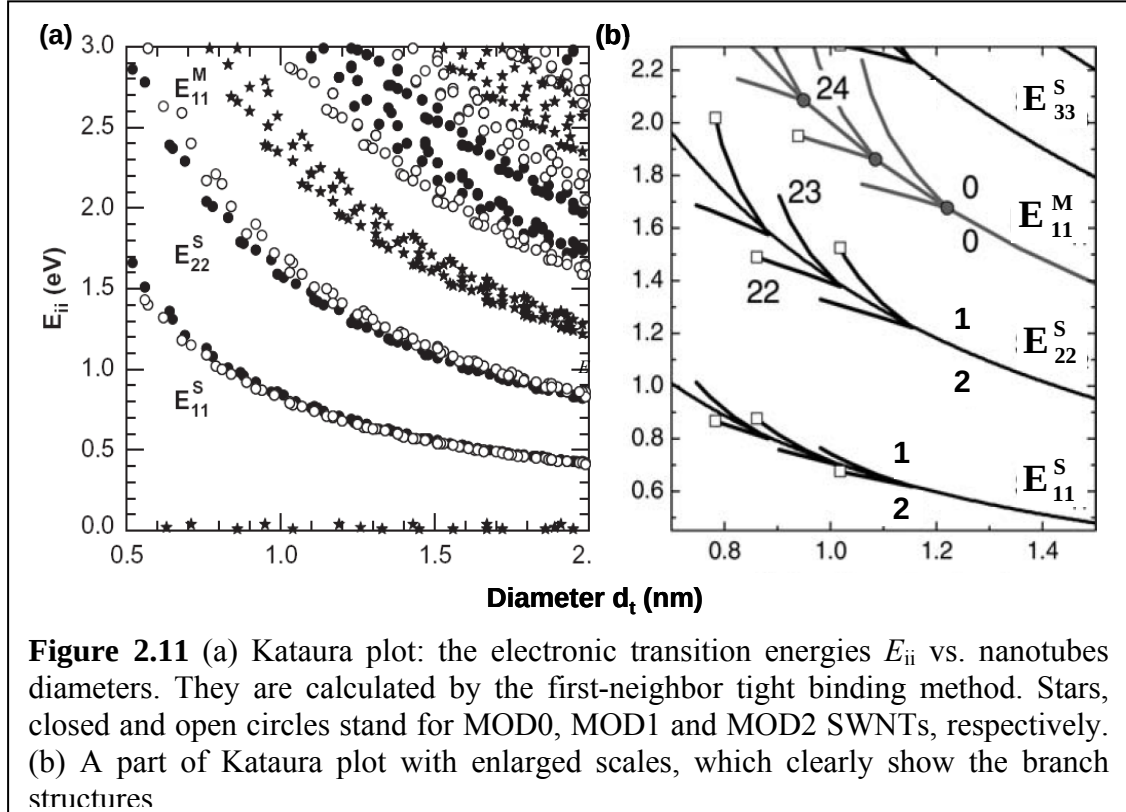
The energy difference between the valence bands  $v_i$  and conduction bands  $c_i$  is called the electronic transition energies  $E_{ii}$  ( $i = 1, 2, 3 \dots$ ). For example,  $E_{11}$  means the transition energy between the highest valence band  $v_1$  and the lowest conduction band  $c_1$ ,  $E_{22}$  for  $v_2 \rightarrow c_2$ , and so on. In the density of states (DOS), it can be indicated as the energy difference from first vHS in valence band to first vHS in conduction band across the Fermi level (Figure 2.10).<sup>47</sup>  $E_{ii}^M$  and  $E_{ii}^S$  are used to stand for transition

energy for metallic and semiconducting tubes. Since each nanotube has a different set of vHSs, which depends on its diameter and chiral angle, the transition energies depend consequently on these two parameters. This makes it



possible to assign the chirality of a tube according to its transition energy.

By plotting the transition energies  $E_{ii}$  vs. tube diameter for all chiral angles, we can obtain the so-called Kataura plot (Figure 2.11), which is named after *Hitomichi Kataura*.<sup>54</sup> From Figure 2.11a, we can see that the transition energies  $E_{ii}^S$  or  $E_{ii}^M$  form the well-separated energy groups, which roughly follow  $1/d_t$  trend. Due to the trigonal warping effect, the energies have systematic deviations from the trend.



In the plot, the three families are indicated by different symbols: open and close circle for MOD1 and MOD2 semiconducting tubes, stars for MOD0 metallic tubes. Figure 2.11b shows a part of the plot on an enlarged scale. From it, we can more clearly see the branch structure, which occurred due to different deviations. The branch number is equal to  $2n + m$ . For example, branch 22 is formed by (11, 0), (10, 2), (9, 4) and (8, 6) tubes from the tip to root. Along the same branch, the diameter of nanotubes decreases with decreasing chiral angle. At same time, the trigonal warping effect increases.

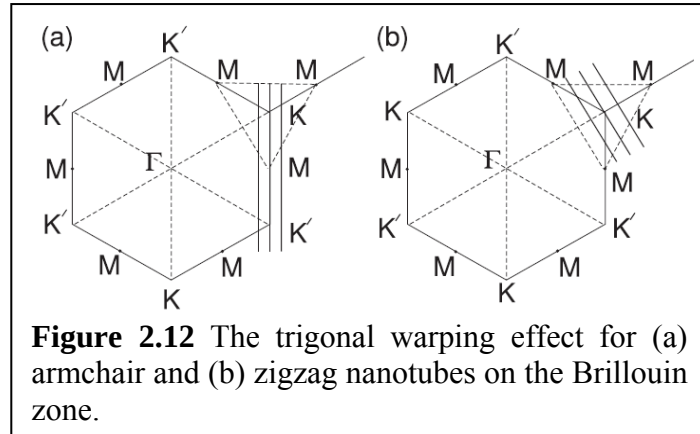
The nanotube properties depends systematically on the family and branch they belong to and the position within one branch. Therefore Nanotube families and branches play an important role in the spectroscopy study below.

#### 2.3.4. Trigonal warping effect

Since the linear  $\mathbf{k}$  approximation is used to calculate the energy dispersion relations of graphite, the transition energy  $E_{ii}$  should depend only on the nanotube diameter  $d_t$ . However in Figure 2.11, the transition energy  $E_{ii}$  deviates from the  $1/d_t$  trend with decreasing diameter and chirality.

Let us go back to the equi-energy contours in Figure 2.7b. We can see the equi-energy contours near  $\mathbf{k}$  points are not circles, but rather exhibit a trigonally warped shape. When the wave vector  $\mathbf{k}$  becomes large, the equi-energy contour becomes a triangle which connects the three M points close to the K point. The distortion of the equi-energy contours away from the circular shape is so-called the trigonal warping effect.

In metallic nanotubes, the trigonal warping effect generally split vHSs, therefore the transition energy of same nanotubes will split into two,  $E_{ii}^H$



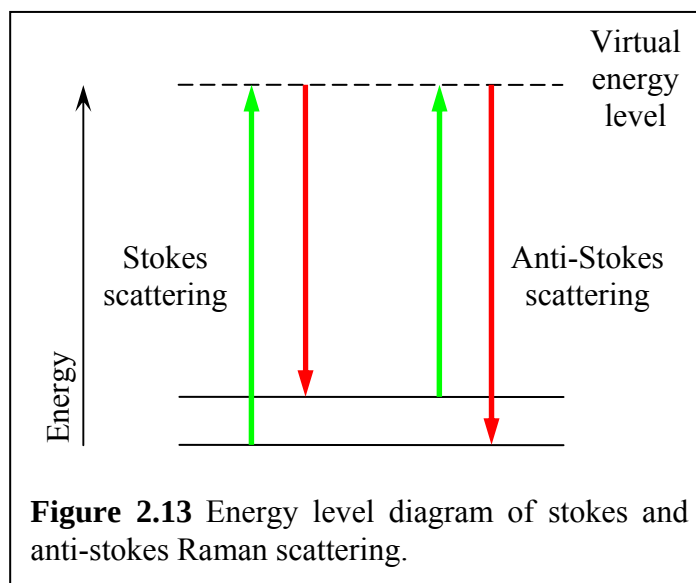
and  $E_{ii}^L$ . However this splitting depends on the chirality of the nanotubes. Figure 2.12<sup>56</sup> shows the cutting lines near a K point for an armchair and zigzag metallic tube. For the metallic tubes, one of the cutting lines will cross the K point. For armchair nanotubes as shown in Figure 2.12a, the two cutting line near the K point, which gives the energy positions of the vHSs, are equivalent to each other, thus the vHSs energies are equal and no splitting for the transition energy. For zigzag nanotubes (Figure 2.12) and chiral nanotubes, the two cutting lines are not equivalent, which gives rise to a splitting of the vHSs energies, further the splitting of the transition energy. The splitting values are a function of the chiral angle.

On the other hand, for semiconducting nanotubes, in which no cutting lines cross the K point, since the two cutting lines near the K point contribute to different transition energy:  $E_{11}^S$  and  $E_{22}^S$ , there is no splitting of the vHSs.

## 2.4. Raman scattering

Raman scattering is the inelastic scattering of a photon, during which an electron is excited by an incident photon and transfers from the electronic ground state to the first electronic excited state. The excited electron loses or gains energy by emitting or absorbing a phonon. Then it emits a photon and relaxes back to the ground state. There are two types of Raman scattering: Stokes and anti-Stokes process. The

energy level diagram of these two scattering processes is shown in Figure 2.13. In Stokes scattering, the molecule obtains energy by absorbing a phonon, while in anti-Stokes process, the molecule loses energy since it emits a phonon.



#### 2.4.1. Resonance Raman scattering

In a non-resonance Raman scattering, the electron is excited from the ground state to a virtual state. Since the process is not in resonance, the non-resonant Raman scattering normally is very weak. On the other hand, in a resonance Raman scattering, rather than excited to the virtual state, the molecule is excited to near one of its real (empty) electronic states. Normally, the intensity for resonance Raman process is  $10^3$  larger than the intensity of non-resonance Raman process.

There are two resonance conditions: incidence resonance and scattered resonance. For the incidence resonance, the optical transition is in resonance with the incident laser photon, which means the incident laser energy  $E_L$  will be same as the energy difference between the two involved electronic states:  $E_L = \Delta E$ . In the scattered resonance, the optical transition is in resonance with the scattering photon. In this case, the laser photon energy has addition energy of the phonon  $\hbar\omega_{ph}$ :

$$E_L = \Delta E + \hbar\omega_{ph}.$$

The first –order Raman intensity can be calculated by

$$I(\omega, E_L) = C \left( \frac{E_a}{E_j} \right) [n(q, \mu) + 1] \sum_j \left| \sum_a \frac{M^d(\mathbf{k} - \mathbf{q}, jb) M^{ep}(\mathbf{q}, ba) M^d(\mathbf{k}, aj)}{(E_L - \Delta E - i\gamma)(E_L - \Delta E - \hbar\omega - i\gamma)} \right|^2,$$

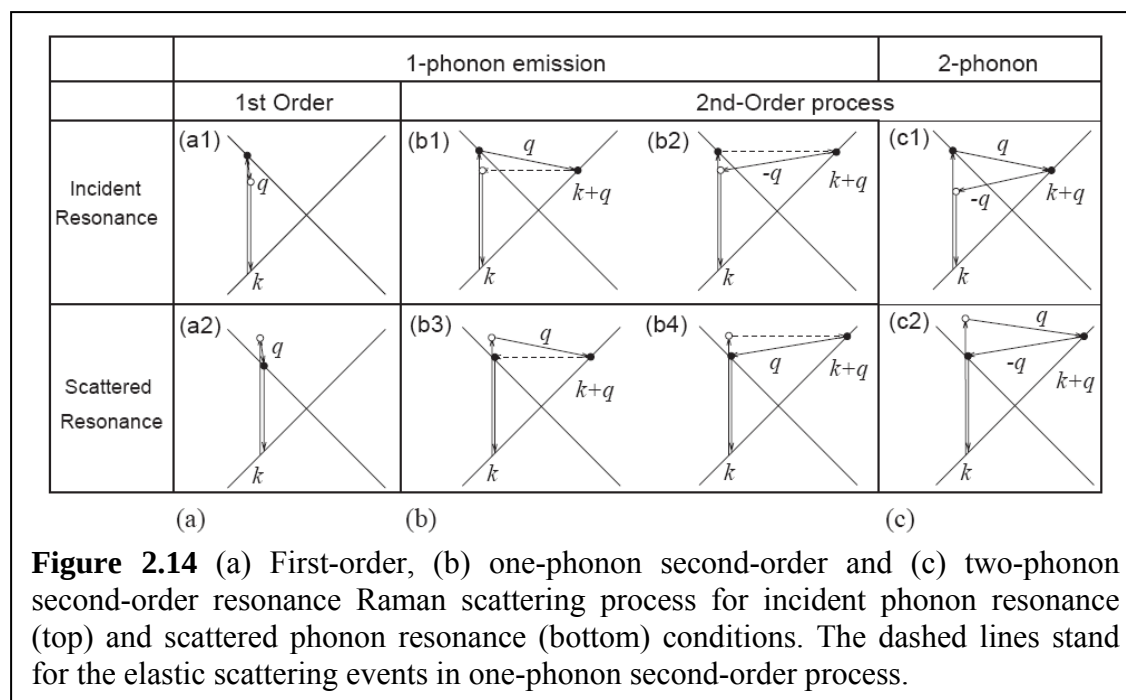
in which  $C$  is a constant independent of  $(n, m)$  chirality,  $n(q, \mu)$  is the number of phonons, and  $\Delta E = E_a - E_j$  ( $a, j$  denote respectively the initial state and excited state). From the equation, the resonance occurs with either  $E_L = \Delta E$  or  $E_L = \Delta E + \hbar\omega$ , where the intensity will reach maximum. In the case of SWNTs, the phonon energies of the G-band (0.2eV) are much larger than that for the RBM (0.02eV). For G band, the two resonance maxima are separated very well, while for RBM, they are very close to each other. Therefore we can observe both G-band and RBM in the incident resonance condition. However, the RBM is not observed when the scattering resonance condition is satisfied for G band.<sup>53</sup>

For SWNT, the Raman intensity is much enhanced not only by the resonance effect but also by the special 1D singularity structure in DOS. When the laser energy is same as the energy difference between vHSs in valence band and conduction band  $E_{ii}$  for a nanotube, the Raman intensity becomes extremely strong. It makes possible to measure the Raman signal from a single SWNT.

#### 2.4.2. First-order and second-order Raman scattering

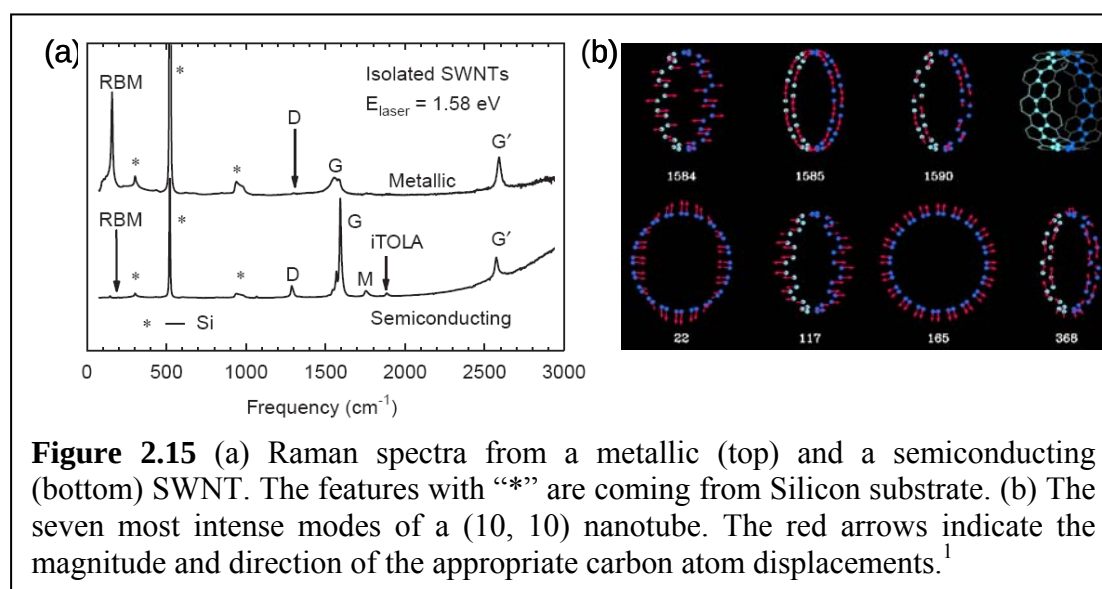
Depending on the number of phonons that the molecule emits before relaxing to the ground state, the Raman scattering can be called one-phonon, two-phonon and multi-phonon Raman processes. On the other hand, the order of Raman scattering is determined by its number in the sequence of the total scattering events. The lowest order process is the first-order Raman scattering which only involves one-phonon emission (Figure 2.14a). For the second-order Raman scattering, it can be either one-phonon or two-phonon process (Figure 2.14b and c). In the second-order Raman

scattering, an elastic scattering, for example change of electron direction but no energy change, will be involved (The dash lines in Figure 2.14b).<sup>53</sup>



### 2.4.3. Raman spectroscopy of single SWNTs

Due to the strong resonance condition, it is possible to measure Raman spectra of SWNTs at single tube level. Figure 2.15a gives a general view of the Raman spectra of a metallic and a semiconducting SWNT.<sup>53</sup> It shows several Raman active features. The two dominant and usually strongest Raman features, which are both the



first-order Raman mode, are the radial breathing mode (RBM) at low frequencies and the tangential (G band) multi-features at higher frequencies. Also the spectra show other weak and higher-order features, such as the disorder-induced D band, the M band (an overtone mode) and the iTOLA band (a combination of optical and acoustic modes).

The RBM is a bond-stretch out-of-plane phonon mode (Figure 2.15b). In this mode, all the carbon atoms move coherently in the radial direction. RBM is a unique phonon mode which only appears in carbon nanotubes. It is often considered as nanotubes' fingerprint. For a single tube, there is only one RBM peak. The RBM frequency  $\omega_{RBM}$  is inversely proportional to the tube diameter  $d_t$ :

$$\omega_{RBM} = A / d_t + B$$

This dependence comes from the fact that the mass of the carbon atoms along the circumferential direction is proportional to the diameter. Due to the effect of the substrate and tube-tube interactions, the A, B constants will be slightly different. A few similar equations have been established in literature.<sup>32,55,57-59</sup> For example, It has been found that  $A = 204 \text{ cm}^{-1}\text{nm}$  and  $B = 27 \text{ cm}^{-1}$  for suspended nanotubes, while for isolated SWNTs on an oxidized Si substrate, it has been found that  $A = 248 \text{ cm}^{-1}\text{nm}$  and  $B = 0$ .

The G-band in carbon nanotubes, which is occurring around  $1500\sim 1605 \text{ cm}^{-1}$ , is carbon-carbon vibrations along the nanotube axis or along the circumferential direction of the SWNT (Figure 2.15b). It is basically derived from the Raman allowed optical mode  $E_{2g}$  of the 2D graphene sheet, which gives two in-plane optical-phonon modes, the longitudinal-optical (LO) and transverse-optical (TO) phonon modes at the  $\Gamma$  point in the two-dimensional Brillouin zone. In SWNTs, they split into two peaks,  $G^+$  and  $G^-$  peaks, respectively.<sup>7,35,60</sup> Due to the curvature effect, the  $G^+$  frequency

does not depend on tube diameter  $d_t$ , but the  $G^-$  frequency decreases with decreasing  $d_t$ .<sup>61</sup> In particular, the  $G^-$  Raman peaks of metallic SWNTs appear at a lower frequency than the  $G^-$  Raman peaks of semiconducting SWNTs with a similar diameter.<sup>62</sup>

Another important aspect of the G-band is the different characteristic line shape between semiconducting and metallic tubes. Generally, isolated semiconducting nanotubes show two dominant Lorentzian peaks. The lower frequency component  $G^-$  is associated with vibrations along the circumferential direction and the higher frequency component  $G^+$  is attributed to vibrations along the tube axis direction. In contrast, the  $G^-$  Raman spectra of metallic SWNTs show a broad and asymmetric Breit-Wigner-Fano (BWF) line shape,<sup>1,54,61,62</sup> which is given by

$$I(\omega) = I_0 \left[ 1 + (\omega - \omega_0) / q\Gamma \right]^2 / \left\{ 1 + [(\omega - \omega_0) / \Gamma]^2 \right\}.$$

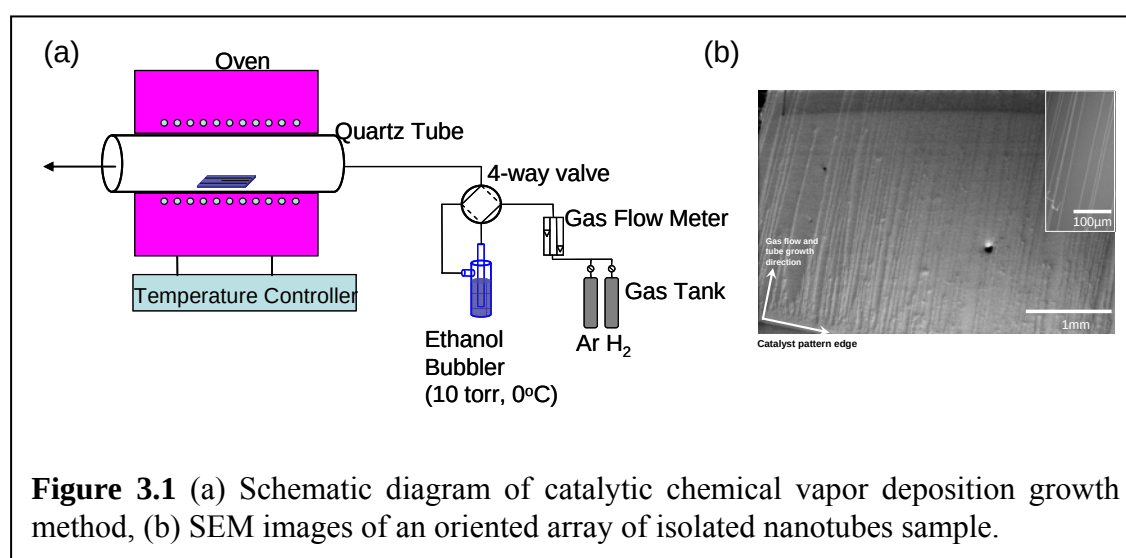
Here  $q$  is the asymmetry parameter. When  $1/q \rightarrow 0$ , the BWF line reduces to a Lorentzian line. Parameter  $\Gamma$  corresponds to the half width at half maximum and  $\omega_0$  is the peak frequency.

## Chapter 3

## Experimental Methods

### 3.1. Sample preparation: CVD growth

Samples consisting of oriented individual carbon nanotubes used in my study were provided by the O'Brien group. They were all grown by controlled CVD with ethanol as the carbon source and a Co thin film as the catalyst, as described previously.<sup>26</sup> The schematic diagram of the CVD growth method is shown in Figure 3.1a. Briefly, Co ultrathin films (0.5-2 nm) were deposited on a silicon wafer, which has a ~200 nm SiO<sub>2</sub> layer, via an e-beam evaporator (Semicore SC2000) with a deposition rate of 0.01 nm/s. Usually a glass slide was used as a mask to deposit Co on only one edge of the substrate surface. The substrate was then placed in the CVD quartz tube furnace and was gradually heated to 850 °C in an Ar/H<sub>2</sub> (520 sccm/65 sccm) flow for 1 hour before ethanol was introduced for nanotube growth. During the heating process, the as-deposited Co ultra thin film is believed to ball up to form individual nanoparticles (2-10 nm in diameter). In typical CVD growth, ethanol with a trace amount of water (0.2-5 wt %) was delivered into the CVD reactor by bubbling



Ar/H<sub>2</sub> mixture gas (10:1 by volume, 60-300 sccm) through an ethanol pool (0 °C). Ultra long nanotubes were found to grow from the Co film along the gas flow direction.<sup>5</sup> The representative SEM images of an oriented array of isolated ultra long nanotubes grown by this CVD method are shown in Figure 3.1b.

### 3.2. Scanning electron microscope

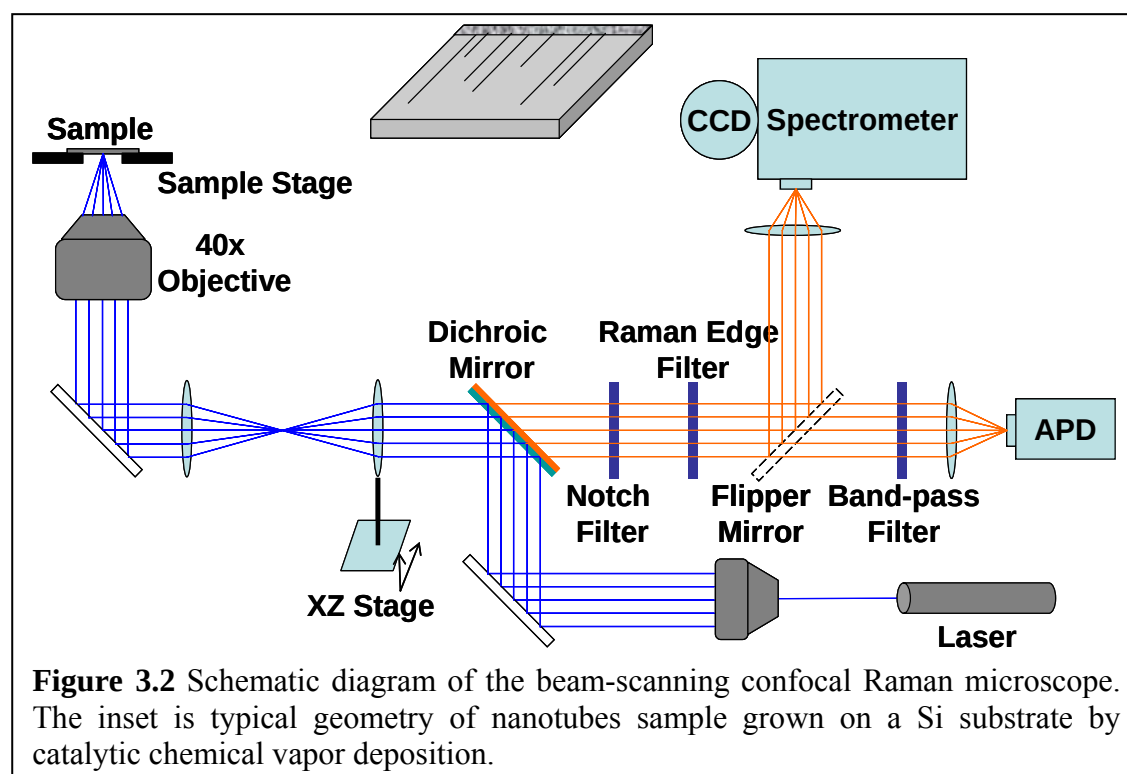
Scanning electron microscope (SEM) was used to image nanotube samples. SEM images of SWNTs grown on Si/SiO<sub>2</sub> substrate were taken on a Hitachi S4700 field emission SEM operated at 0.8 kV. The low resolution SEM images were usually taken before the Raman study in order to provide a view of nanotube density on the substrate. For some samples, after Raman characterization, a series of high resolution SEM images of ~200 μm x 100 μm area were taken consecutively along the catalyst region across the substrate, as in Figure 3.1b. These SEM images were used to compare to the corresponding Raman images subsequently.

### 3.3. Laser scanning confocal Raman microscope

A laboratory-designed confocal microscope was used for Raman imaging and spectroscopy measurement at the single nanotube level.<sup>46</sup> The microscope is based on a beam-scanning scheme, as shown schematically in Figure 3.2. The excitation laser (633 nm, 594 nm, 543nm or 514nm) was focused to a spot of ~800 nm in size on the sample plane by a microscope objective (Nikon 40x, NA 0.6). The Raman scattering signal was collected by the same objective, transmitted through the dichroic beam splitter, and detected by an avalanche photodiode (APD, Perkin-Elmer SPCM-AQR-15). The Laser Rayleigh scattering and the Si substrate background Raman scattering were blocked by using a notch filter, a Raman edge filter, and a band-pass filter

centered at the SWNTs G-band Raman peak. The transmission wavelength range of these Filters (Kaiser, Semrock or Andover) must be consistent with the used excitation wavelength.

To image nanotubes, the focused laser spot was raster-scanned over the sample plane by continuously translating the first lens after the dichroic mirror in the



plane perpendicular to the optical axis. The second identical lens, which acts as the tube lens for the infinity-corrected objective, recollimates the laser beam to fill the entrance aperture of the objective. The distances from the tube lens to the scanning lens and to the entrance aperture of the objective are both equal to twice the focal length of the tube lens. Therefore the deflected incoming laser beam always fills the entrance aperture of the object during scanning. In order to adjust the laser beam focusing onto the sample plane, the objective is mounted on a Z-stage.

Because of the magnification of the microscope objective, the translation stage (Melles Griot, Nanomover) used to move the scanning lens does not need a high resolution. A translating repeatability of 1  $\mu\text{m}$  for the stage implies a laser positioning

repeatability of 25 nm on the sample plane if a 40x objective is used. This high repeatability allows for fast laser spot positioning to a single nanotube after the Raman image is acquired. The typical scan area was 100  $\mu\text{m}$  x 100  $\mu\text{m}$ , and the integration time was 15ms for each step. The sample was mounted on a mechanical translational stage so that the sample could be scanned systematically and sequentially across the entire substrate edge near the deposited catalyst.

Raman spectra of imaged SWNTs were measured by a liquid nitrogen-cooled CCD camera (Princeton Instruments) attached to the spectrograph (Acton), with typical exposure times of 2-5 min. In order to avoid laser heating, the excitation laser power was kept less than 3 mW. Therefore the actual laser power reaching sample surface was less than 1 mW. The entire imaging and positioning process was controlled by Labview software (National Instrument).

The ultra long nanotubes protruding from the catalyst region are the focus of the study. The sample was positioned in such a way that the long nanotubes were perpendicular to the fast scanning axis. In this way, only a few scans starting from the catalyst film were necessary in order to determine whether any ultra long nanotubes were present in the Raman imaging. By this strategy we were able to systematically image the large area along the catalyst film, typically 5-10 mm long, on different samples. Hundreds of isolated SWNTs that satisfy resonance Raman conditions were imaged and mapped from these samples.

## Chapter 4

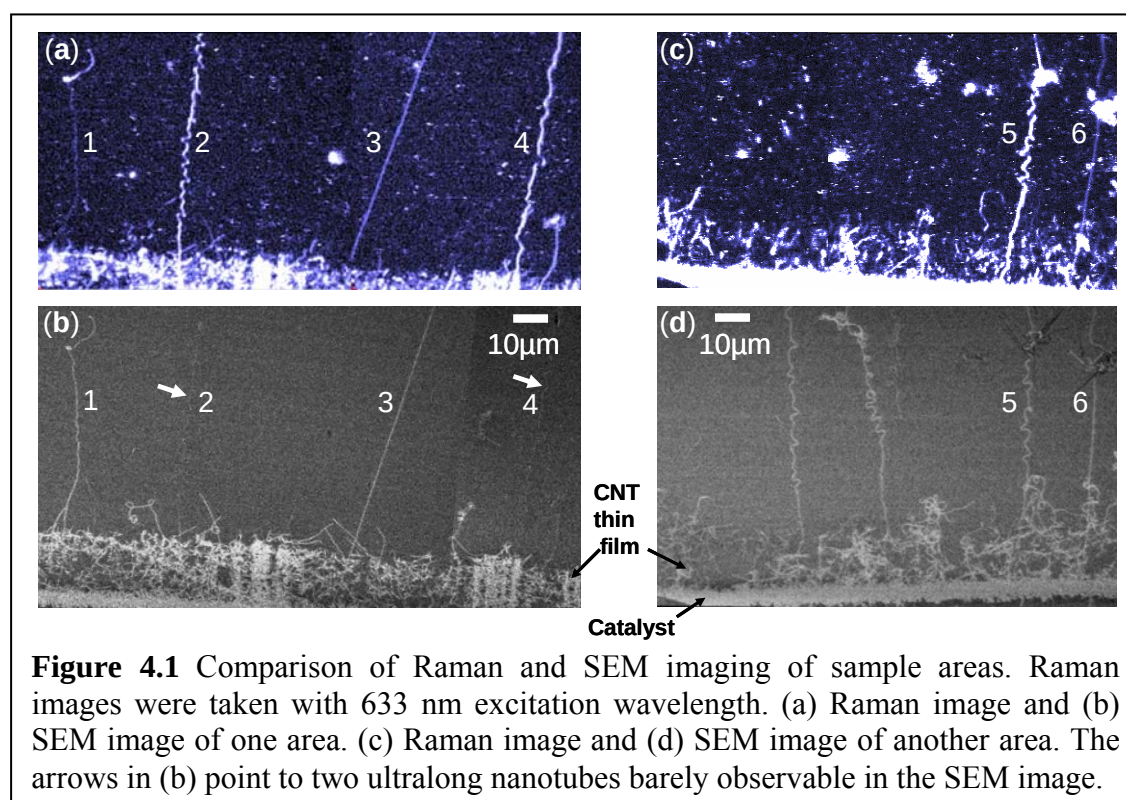
### Raman imaging and first-order Raman spectroscopy

The two main Raman-active features of SWNTs are the radial breathing mode (RBM) at low frequency and the high-frequency tangential mode (G band). The RBM has been used to determine the tube diameter  $d_t$  and relative populations of different diameter nanotubes in a bulk sample, since the RBM frequency  $\omega_{\text{RBM}}$  is inversely proportional to the tube diameter (but not chirality).<sup>32,63,64</sup> Optical transition energies  $E_{ij}$  have been determined from the RBM resonance Raman excitation profile<sup>65,66</sup> and the RBM anti-Stokes/Stokes Raman intensity ratio.<sup>36,67,68</sup> By combining  $d_t$  and  $E_{ij}$ , we are able to assign  $(n, m)$  indices to the observed Raman peaks. On the other hand, the Raman spectral line shape of the G band has been shown to strongly depend on the electronic type of nanotubes. Metallic tubes exhibit broadened G band Raman spectra, which can be fitted by an asymmetric BWF line shape, while semiconducting tubes show sharp Lorentzian line shape.

In this chapter, I will show the single nanotube Raman characterization work at room temperature. We used the beam-scanning confocal Raman microscope to map SWNTs grown on large Si/SiO<sub>2</sub> substrates of ~10mm lateral dimension. We compare Raman imaging with SEM imaging of the same sample to illustrate the imaging capability of our Raman microscopy system. Raman spectra for more than 200 long nanotubes are collected in this work. Variation in RBM Raman intensity and G band Raman line shape of individual nanotubes are observed and discussed. Tube diameters determined from RBM frequencies reflect a broad diameter distribution ranging from 0.8 to 2 nm for CVD grown nanotubes.

### 4.1. Raman imaging

Normally, Raman imaging of SWNTs was performed prior to high resolution SEM imaging to avoid potential damage to SWNTs from excess exposure to electrons in SEM imaging that might influence the Raman spectra. As I mentioned in the last chapter, the band pass filter is centered on the G band frequency, thus our Raman imaging is based on the G band signal detection.



In Figure 4.1, both Raman images and SEM images of two representative areas on a nanotube sample are given. From the images, we can see there are three regions of variable nanotube growth density which can be easily identified on each sample. The catalyst region yields the strongest intensity in both Raman imaging and SEM imaging, which is due to the presence of high-density nanotubes and possible photoemission from the catalyst. Next to the catalyst area is the nanotube thin film region consisting of short entangled nanotubes. The third area consists of well-separated ultra long nanotubes that are seen to protrude from the nanotube thin film.

We focus our imaging and Raman spectra measurement on these isolated ultralong tubes.

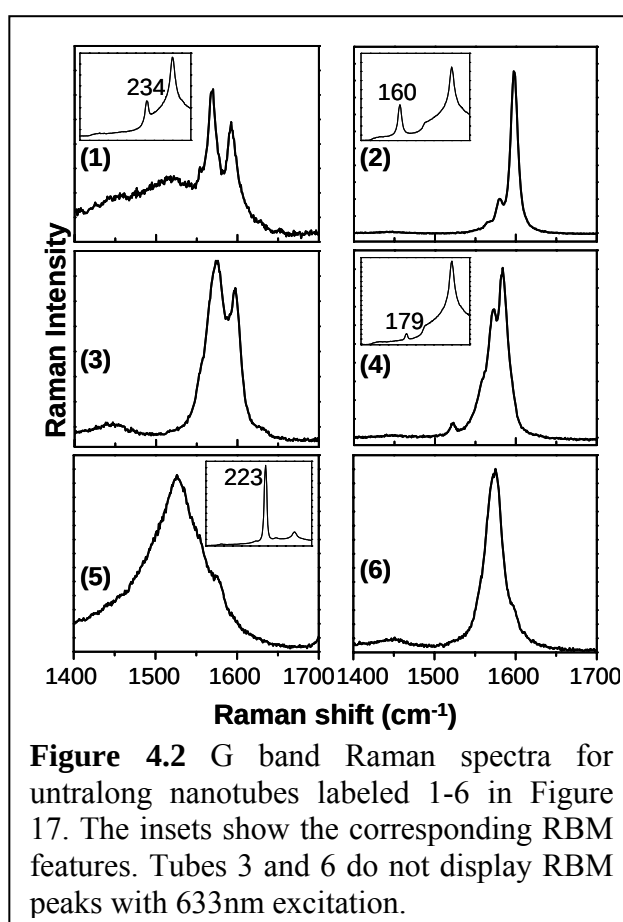
In the experiment, by using the irregular features in the catalyst area and the nanotube thin film region as markers, we are able to match all Raman images to the corresponding SEM images of the same areas. For example, Figure 4.1a-b are Raman and SEM images of one area. All four nanotubes seen in the SEM image (Figure 4.1b) can also be identified in the Raman image (Figure 4.1a). In fact, among all four tubes, tube 2 and 4 are weak and barely observable in SEM imaging, but they appear to be intense in Raman imaging. For another area shown in Figure 4.1c and d, at least four long tubes are visible in the SEM image, but only two of them, tube 5 and 6, are revealed in the Raman image. Apparently it is caused by the resonance enhancement condition for observing single tube Raman scattering. Raman imaging can reveal only those nanotubes whose electronic transition energies  $E_{ii}$  are in resonance with the incident or scattered photons. By carefully examining both SEM and Raman images for two samples, we found that about 60% of the ultra long tubes seen in SEM imaging also appear in G-band Raman imaging under 633nm excitation. By using different wavelength excitation laser, all nanotubes should be observed.

In the experiment, the linear polarization of the excitation laser was adjusted to be along the nanotube growth direction (nanotube axial direction) in order to achieve maximum Raman intensity.<sup>69-71</sup> In Figure 4.1a and 4.1c, straight nanotubes, like tube 3, show uniform Raman intensity along the tube length, which is expected from the fact that Raman scattering of SWNTs depends on the excitation polarization. On the other hand, the twisted nanotubes, such as tube 2 and 5, are observed to display variable Raman intensity along their tube direction. It is obviously caused by the variation in the angle between laser polarization and nanotube axis direction.

## 4.2. Raman spectra of individual SWNTs

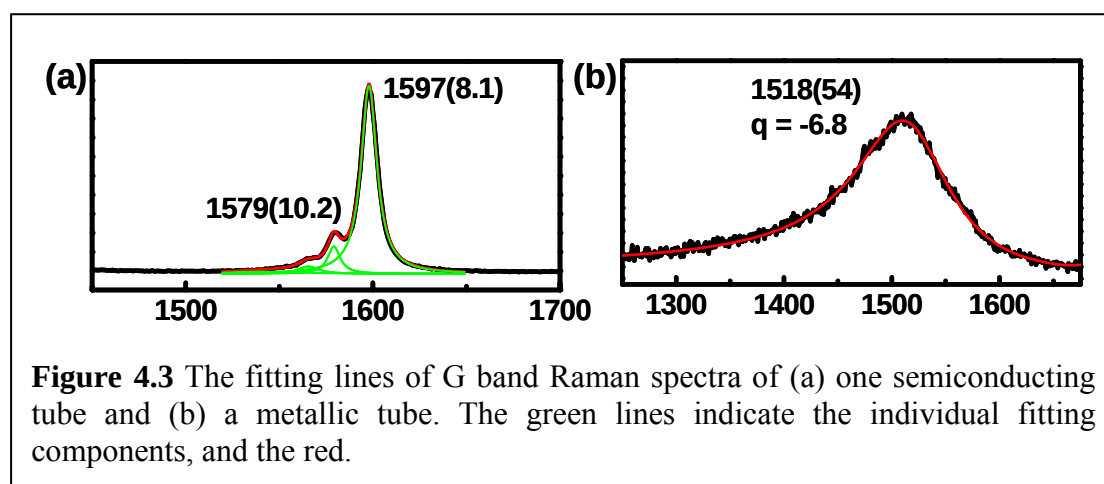
Figure 4.2 shows the Raman spectra for tubes 1-6 highlighted in Figure 4.1. As I mentioned in the background section, RBM and G mode have different resonance windows. Not all nanotubes appearing in G band Raman imaging will display RBM peaks. In this work, we carefully examined Raman spectra of ~200 individual nanotubes imaged by G band Raman scattering. Among them, only 95 tubes exhibit RBM modes, consisting of both metallic and semiconducting tubes. In Figure 4.2, tubes 3 and 6 do not exhibit RBM peaks under 633nm laser excitation.

The line shapes of G band spectra of these six tubes are quite different. For instance, tube 2 shows a typical semiconducting-type G-mode Raman spectrum with relatively sharp Lorentzian line shape. The other five tubes



show metallic-type G-mode Raman spectra, with different extents of line broadening. Among them, tube 5 exhibits an asymmetric broad BWF component at  $1526\text{ cm}^{-1}$  in the G band spectrum. The G band spectra of semiconducting tubes usually can be fitted by 2-4 Lorentzian peaks, while that of metallic tubes can be fitted by a BWF peak. Sometimes, the inclusion of additional Lorentzian peaks is necessary for G band

spectra of metallic tubes. Examples of G band spectra fitting for one semiconducting tube and one metallic tube are shown in Figure 4.3, which highlights the very different G band spectra of these two types of tubes. For the semiconducting tube (Figure 4.3a), its G band spectrum is fitted by three Lorentzian peaks. The peak frequency and full width at half maximum (FWHM) of two major peaks are labeled in the figure. For the metallic tube (Figure 4.3b), one BWF peak is sufficient to fit the whole G band spectrum. The peak frequency, half width at half maximum and the asymmetric parameter  $q$  are also given in the figure.



### 4.3. Structure assignment

In order to compare the RBM intensity for nanotubes showing RBM Raman peaks, the RBM intensity of each nanotube is first normalized by the  $303\text{ cm}^{-1}$  Raman peak of the Si substrate. Then the normalized RBM intensity for 95 tubes is plotted against their RBM frequency under 633nm excitation, spanning from at least  $135\text{ cm}^{-1}$  up to  $285\text{ cm}^{-1}$  (Figure 4.4b). As expected, RBM Raman intensity is observed to generally decrease with increasing nanotube diameter.

In order to identify the  $(n, m)$  chiral indices for these 95 nanotubes, a plot of the optical transition energies  $E_{ii}$  for different nanotubes against their inverse diameter

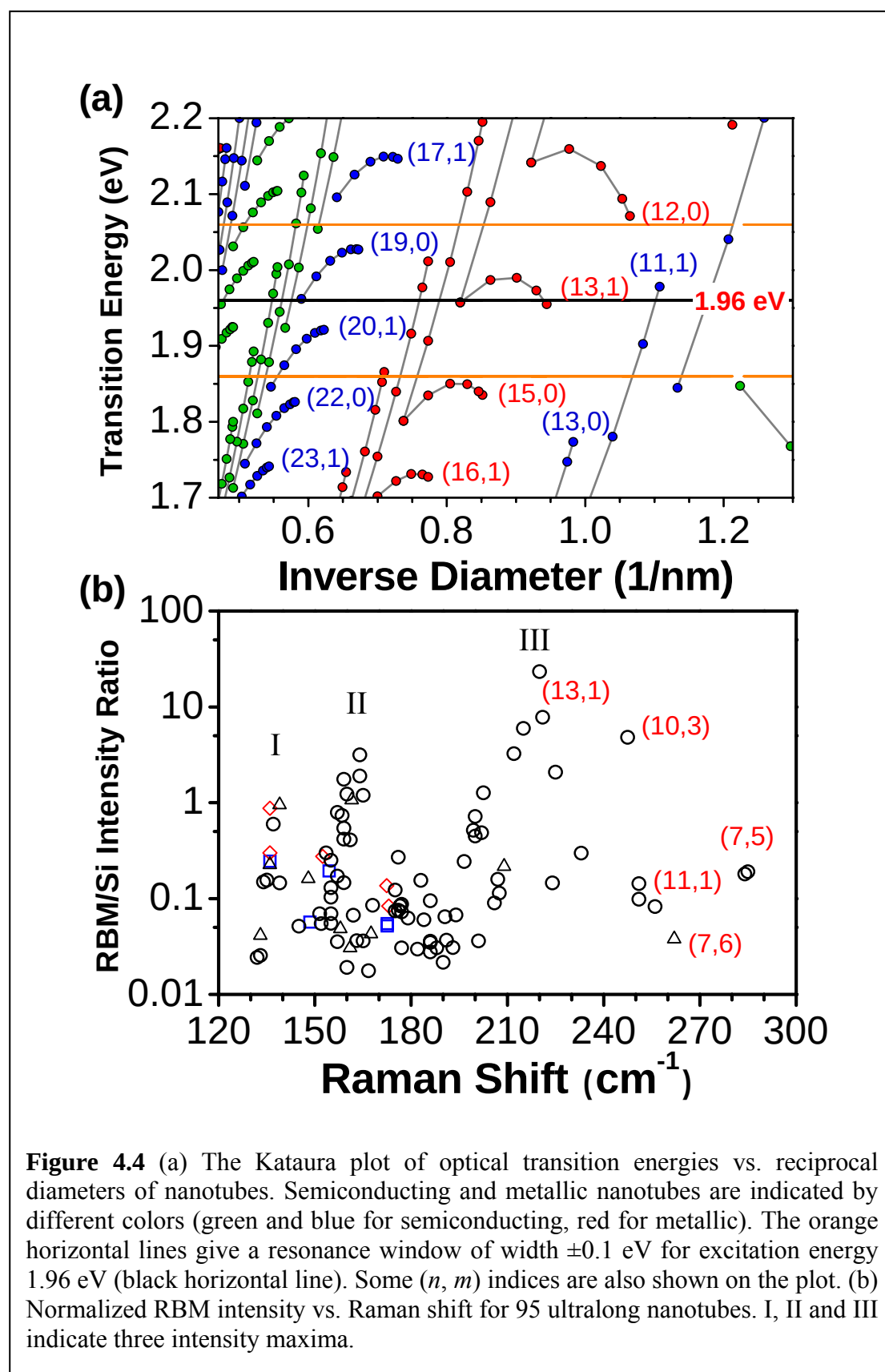


**Figure 4.4** (a) The Kataura plot of optical transition energies vs. reciprocal diameters of nanotubes. Semiconducting and metallic nanotubes are indicated by different colors (green and blue for semiconducting, red for metallic). The orange horizontal lines give a resonance window of width  $\pm 0.1$  eV for excitation energy 1.96 eV (black horizontal line). Some (n, m) indices are also shown on the plot. (b) Normalized RBM intensity vs. Raman shift for 95 ultralong nanotubes. I, II and III indicate three intensity maxima.

is used. This plot, shown in Figure 4.4a, is called Kataura plot. This Kataura plot is adapted from the work by Son et al.,<sup>40</sup> which was calculated by the extended tight-

binding (ETB) method<sup>72</sup> and found to agree well with the experimental  $E_{ii}$  values for isolated tubes dispersed in water. The transition energies  $E_{ii}$  of nanotubes have been shown to depend on the dielectric environment surrounding the nanotubes.<sup>65</sup> Son et al. also determined the transition energies for both semiconducting and metallic nanotubes grown on Si by measuring the resonance Raman excitation profile.<sup>73</sup>  $E_{ii}$  for tubes on the Si substrate was found to be on average  $\sim 70$  meV lower than ETB calculation. Thus the calculated transition energies in Figure 4.4a have all been downshifted by 70 meV from the original data by Son et al. Also in Figure 4.4a, the red circles correspond to metallic tubes, while the green and blue ones stand for MOD1 and MOD2 semiconducting nanotubes. Due to the trigonal warping effect,<sup>74</sup> the optical transition energy  $E_{11}^M$  of a non-armchair metallic tube splits to low-energy branch  $E_{11L}^M$  and high-energy branch  $E_{11H}^M$ .

It has been established that RBM frequency of a nanotube depends only weakly on its surrounding environment. The RBM frequencies of nanotubes with the same  $(n, m)$  structure have been shown to be very close for tube dispersed in water, in bundles, or grown on a substrate.<sup>55,59,66,75</sup> A few equations relating nanotube diameter  $d_t$  to its RBM frequency  $\omega_{\text{RBM}}$  have been established in literature. The most recent one by Araujo et al.<sup>55</sup>,

$$\omega_{\text{RBM}} = 217.8/d_t + 15.7, \quad (4.1)$$

shows an agreement for a broad diameter range of nanotubes grown on a quartz substrate (0.7–2.2 nm). Therefore this equation is used in the present study to convert RBM frequency to the tube diameter, and then we are able to assign  $(n, m)$  chiral index to the observed RBM Raman peaks.

Since only a few  $(n, m)$  structures are possible within the resonance window for high RBM frequencies ( $>220 \text{ cm}^{-1}$ ), these peaks can be assigned satisfactorily by

comparison with the predicted RBM frequencies from the equation. For example, as shown in Figure 4.4b, the RBM peak at  $283\text{ cm}^{-1}$  is assigned to a (7, 5) tube, and the intense  $249\text{ cm}^{-1}$  RBM peak is assigned to a (10, 3) tube. They both exhibit sharp semiconducting-type G band Raman spectra.

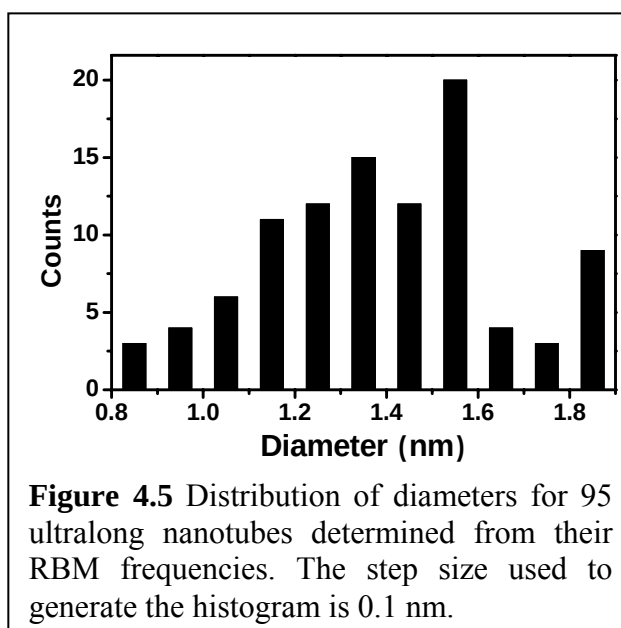
Figure 4.4b also shows that RBM Raman intensity varies periodically with RBM frequency under 633nm laser excitation, with maxima highlighted by I, II, and III. For intensity maximum III at  $\sim 221\text{ cm}^{-1}$ , the RBM Raman signal is about 10 times stronger than the Si  $303\text{ cm}^{-1}$  peak, implying a strong resonance enhancement condition. Its corresponding G mode Raman spectrum, shown in Figure 4.2 as tube 5, has a very broad BWF line shape, suggestive of a metallic tube. Among metallic tubes of the branch 27 ( $2n + m = 27$ ) whose transition  $E_{11L}^M$  are in resonance with the excitation laser, the (13, 1) tube gives a predicted  $\omega_{\text{RBM}}$  of  $221\text{ cm}^{-1}$ . The intense RBM peak at  $221\text{ cm}^{-1}$  is therefore assigned to (13, 1) structure. The observed RBM frequencies from  $221$  to  $176\text{ cm}^{-1}$  are all assigned to metallic tubes. The exciton-phonon coupling matrix element has been predicted to decrease with increasing chiral angle.<sup>76,77</sup> This explains the observed decreasing RBM intensity for metallic tubes whose RBM frequencies are from  $221$  down to  $\sim 190\text{ cm}^{-1}$ . For metallic tubes with  $\omega_{\text{RBM}} < 190\text{ cm}^{-1}$ , the higher branch of metallic transition  $E_{11H}^M$  is involved in resonance Raman scattering. The observed RBM Raman intensity for these tubes typically is very weak, consistent with theoretical prediction<sup>78</sup> and other experimental observations<sup>40</sup> regarding Raman scattering involving  $E_{11H}^M$ .

RBM frequencies smaller than  $170\text{ cm}^{-1}$  are assigned to large semiconducting tubes within the resonance window under 633nm excitation, where resonance Raman scattering is associated with the  $E_{33}^S$  transition. RBM intensity maximum II, at  $\sim 164\text{ cm}^{-1}$ , is assigned to (19, 0) or (18, 2) tubes, which are zigzag or zigzag-like structure

and therefore should have large electron-phonon matrix elements. Similarly, the RBM intensity maximum I, at  $\sim 136 \text{ cm}^{-1}$ , is assigned to (23, 0) or (22, 2) tubes with near-zigzag structure. The predicted RBM frequency is  $\sim 135 \text{ cm}^{-1}$  for these two tubes. Due to the large number of possible structures and uncertainty in the measured  $\omega_{\text{RBM}}$  ( $\pm 2 \text{ cm}^{-1}$ ), it is practically difficult to assign a definite  $(n, m)$  structure to these low RBM frequencies. In order to assign  $(n, m)$  indices to the other observed RBM peaks between intensity maxima I and III, all possible  $(n, m)$  structures in this range within the resonance window have to be included, which demonstrates that there is no preferential growth for specific nanotube structures in the CVD process.

#### 4.4. Diameter distribution of CVD growth

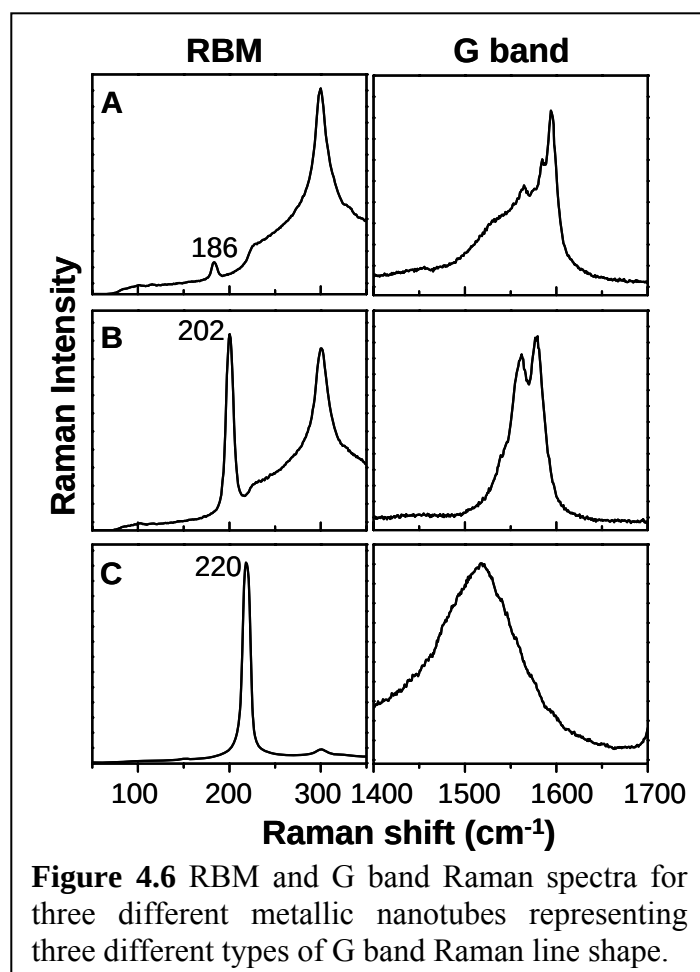
By using equation (4.1), we are able to determine the diameter of SWNTs from their RBM frequencies. The diameter distribution of 95 ultra long nanotubes that show RBM Raman peaks under 633nm excitation is shown in Figure 4.5. The distribution is peaked at  $d_t = 1.5 \text{ nm}$  and ranges from 0.8 nm to 1.9 nm. A dip is observed at 1.6-1.7 nm in the diameter distribution. The diameter distribution obtained for ultra long tubes in the present study appears much broader than that previously reported for CVD grown ultra long tubes<sup>38</sup> but agrees well with the diameter distribution of shorter tubes obtained in the same report.



#### 4.5. G band spectra of metallic nanotubes

In Figure 4.2, there are five metallic tubes (1, 3-6) which all show broad G band peaks. However the broadening of the peak is quite different. In fact, the G band peak of metallic tubes exhibits varying degrees of broadening in our work. Figure 4.6 shows three different types of G-band Raman spectra for metallic nanotubes along with their RBM Raman spectra. In type A, the G band consists of both a broad BWF peak and a few sharp Lorentzian peaks. The BWF peak has a full width at half maximum (FWHM) around  $40\text{ cm}^{-1}$ , but the peak intensity is usually weaker than the main Lorentzian peak at  $\sim 1590\text{ cm}^{-1}$ . In type C, the G band Raman spectrum shows a broad and intense BWF feature and the sharp Lorentzian peaks are barely observable. The FWHM of the BWF peak at  $1519\text{ cm}^{-1}$  in this case reaches  $100\text{ cm}^{-1}$ . The B type metallic nanotubes give a special line shape for G band Raman spectrum, in which the

BWF feature is diminished and the spectra can be fitted by a weak BWF peak and two Lorentzian peaks with FWHM of  $10\text{-}20\text{ cm}^{-1}$ , which is broader than typical semiconducting G band line width ( $\sim 8\text{ cm}^{-1}$ ). Most of the metallic tubes in this work are observed to display type-B G band Raman spectra. We must emphasize that the B-type G band Raman spectra

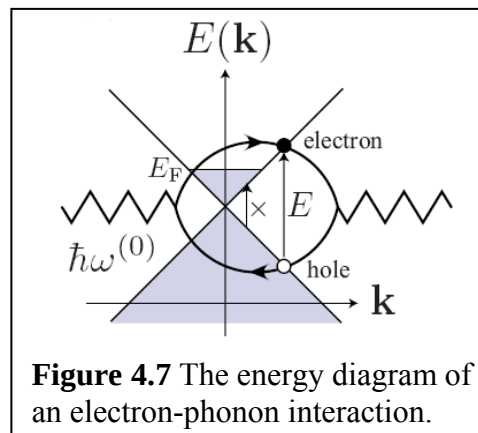


are different from typical semiconducting-type G band Raman spectra. Type-B spectra consist of much broader Lorentzian peaks and the two components at 1590 and 1575  $\text{cm}^{-1}$  have similar amplitudes. Our B-type G band Raman spectrum agrees with the previously observed G band Raman spectra for suspended freestanding metallic tubes<sup>79</sup> and for isolated tubes dispersed in sodium dodecyl sulfate (SDS) solution.<sup>80</sup>

The origin of the BWF feature in metallic G-band Raman spectra was a subject of much debate. Brown et al.<sup>81</sup> proposed that BWF peak was due to coupling of the discrete tangential mode phonon (TO) to the acoustic plasmons facilitated by the nanotube curvature. Recent work involving both TEM and Raman measurement revealed that the BWF feature is enhanced in bundles but is diminished for isolated individual metallic nanotubes,<sup>79,82</sup> supporting an alternative mechanism proposed by Kempa<sup>83</sup> in which the BWF arises from phonon coupling to gapless plasmon modes that are strongly enhanced by bundle formation. However, it has been shown that the BWF feature is significantly influenced by the charge transfer effect.<sup>84,85</sup> Shim et al.<sup>85</sup> demonstrated that the BWF feature of individual metallic nanotubes could be induced by absorption of an electron-donating polymer, poly(ethylenimine) (PEI). Blackburn et al.<sup>80</sup> recently discovered that surfactants with electron-donating groups, such as cholate, tend to enhance the BWF feature for isolated tubes dispersed in surfactant solution. Our observation of diminished BWF feature for isolated metallic tubes on Si wafers in air is consistent with a very recent report by Nguyen et al.,<sup>86</sup> in which the B-type spectrum was attributed to O<sub>2</sub> adsorption, which causes the Fermi level shift. They also observed gradual evolution of single metallic tube G band Raman from a narrow Lorentzian line shape to a broadened BWF line shape by shifting the Fermi

level using electrochemical gating, supporting the idea that the BWF line shape is intrinsic to single metallic tubes but is sensitive to charge transfer.

Recently it has been widely accepted that the origin of BWF line shape of metallic nanotubes is due to the interaction of discrete phonon states with continuous free-electron states, which is shown in Figure 4.7.<sup>87</sup> Since the Fermi level will affect the population of electron-hole pair, this electron-phonon interaction will be



influenced by the Fermi level, which may shift due to O<sub>2</sub> absorption. The charge on the surface of Si wafer also can change the Fermi energy.

The Fermi energy dependent electron-phonon interaction in metallic tubes will be discussed in next chapter.

## Chapter 5

### Charge doping effect on Raman spectra of SWNTs

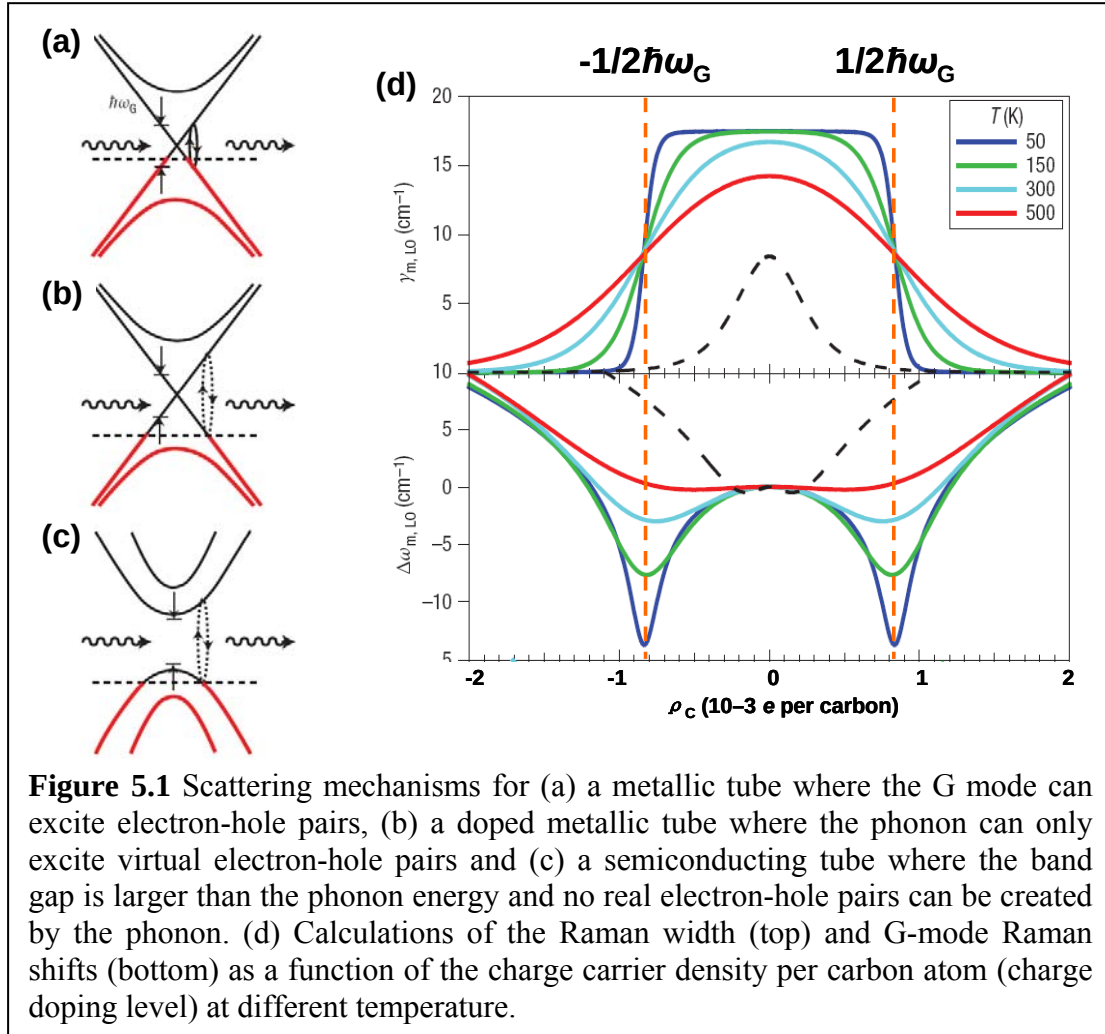
It is shown in chapter 4 that the G band Raman feature of metallic SWNTs often displays a broad asymmetric line shape that can be fitted by a BWF function. This broadened BWF peak has often been used as a signature of metallic tubes that are present in the probed volume. However, it has been shown that the characteristics of the G band spectra of metallic tubes depend sensitively on extrinsic factors such as charge transfer doping induced by molecular adsorption,<sup>84,85,88,89</sup> electrochemical or electrostatic gating.<sup>86,90-94</sup> G-band Raman spectra with narrow line width similar to those in the typical semiconducting tubes have been observed in unintentionally or intentionally doping metallic tubes.<sup>79,86</sup> The same (n, m) metallic tubes species can exhibit very different G band Raman spectra due to the variation in the degree of charge transfer doping.<sup>91</sup>

Also the data shows that O<sub>2</sub> adsorption can influence the Raman spectra of metallic SWNTs via oxidative doping. However in this case, the doping of metallic SWNTs is unintentional and hard to control. In order to study the electron-phonon coupling in metallic tubes, it is desirable to be able to well control the charge doping level of metallic nanotubes. Therefore in the present work, we examined the G band Raman spectra change of metallic tubes, whose Fermi level is controlled by electrostatic and electrochemical gating.

#### 5.1. Electron-phonon coupling

The electron-phonon interaction plays a very important role in broadening of metallic nanotubes. This electron-phonon coupling, which is caused by Kohn anomaly

(KA) at the  $\Gamma$  point in the phonon dispersion, will not only broaden G band Raman spectra of metallic tubes, but also soften the phonon energy. However KA occurs only in the LO phonon mode because the LO phonon distorts the lattice so that a dynamic band gap is induced in the electronic band structure. This lowers the energy of the valence electrons near the Fermi point and thus lowers the energy required to distort the lattice, leading to LO phonon softening.



The electron-phonon coupling mechanism is sensitive to the Fermi energy.<sup>87,92</sup>

As shown in Figure 5.1, when the Fermi level of a metallic tube is close to the band cross point (Figure 5.1a), the G mode phonon can excite electron-hole pairs, which gives rise to the broadening of the Raman signal and shifting of G band frequency. However for a highly doped metallic tube (Figure 5.1b), the phonon can only excite

virtual electron-hole pairs. In this case, the coupling will also lead to the phonon frequency shift, but no broadening. For semiconducting tubes, the band gap is always larger than the phonon energy, and no real electron-hole pairs can be created by the phonon. Therefore the phonon frequency will change and the line width is unchanged with Fermi level.

The calculated numerical results for Raman shift and line width for metallic nanotubes are also shown in Figure 5.1d.<sup>92</sup> The line width has a maximum at zero doping level corresponding to Fermi level at the band cross point. When the Fermi level is moved away from the band cross point, the line width gradually becomes smaller. For the LO peak frequency, the change is a little bit more complex. When the Fermi level is located between  $-1/2\hbar\omega_G$  and  $+1/2\hbar\omega_G$ , the Raman frequency downshifts with the increased doping level. At  $\pm 1/2\hbar\omega_G$ , the frequency will reach two same minima. After that, the  $G^-$  peak will shift back to higher frequency with increasing doping. The Raman frequency and the line width are also predicted to show temperature dependence in Figure 5.1d. At low temperature, the decreasing of the line width becomes steep. At same time, the two minima of the Raman frequency will become sharp and clear.

## 5.2. Electrostatic doping

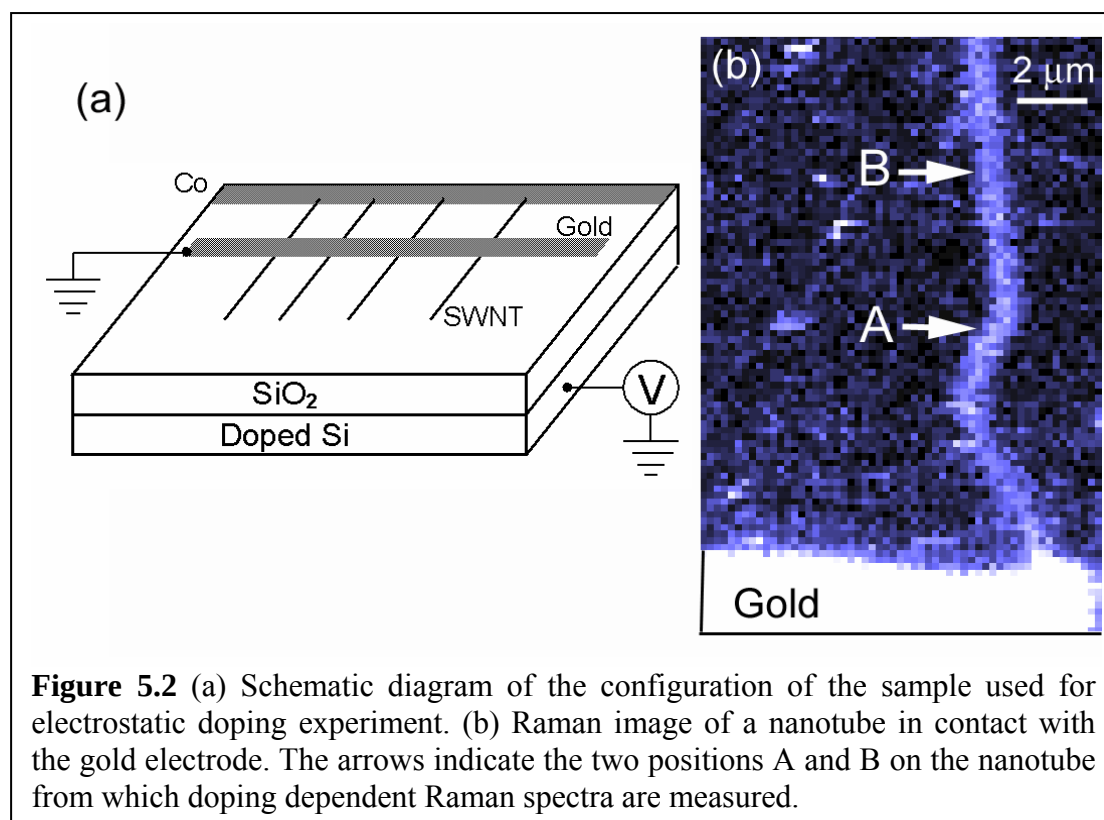
Raman characterization of SWNTs is often carried out in ambient air. When a field-effect transistor (FET) consisting of SWNTs on a Si/SiO<sub>2</sub> substrate is operated in ambient air, it is well known that the conductivity of semiconducting nanotubes exhibits considerable gate hysteresis. This hysteresis is believed to arise from the injection of charges from the nanotube to the charge traps on the SiO<sub>2</sub> oxide, induced by gate potential and assisted by the adsorbed water layer.<sup>95-97</sup> While this effect is

undesirable for nanotube-based FET devices, it provides a means to obtain highly doped metallic SWNTs for the study of electron-phonon coupling in metallic tubes, as will be shown in the present work. It therefore should be interesting and also is important to examine the G band Raman spectra of metallic tubes exposed to ambient air and under electrostatic gating.

In the present work we use the confocal Raman microscopy to investigate the electrostatic doping induced phonon shift of individual metallic SWNTs lying on a Si/SiO<sub>2</sub> substrate that is exposed to ambient air. In agreement with the previous reports,<sup>86,91-93</sup> we find that the G band Raman spectra of a metallic tube in air can change dramatically depending on the applied gate voltage. Very sharp semiconducting-type G band spectra are observed for the highly doped metallic tube. Although the gate-dependent spectral shift is irreversible and shows a hysteresis behavior in the present work, the magnitude of such spectral shift is much larger than reported previously in a similar Raman study of tubes placed in vacuum.<sup>92</sup> This allows us to follow the evolution of Raman spectrum of the metallic tube in a wide range, including the transition from the sharp semiconducting-type line shape to the typical broad BWF line shape.

### 5.2.1. Experimental section

The structure of the sample used in this work is schematically shown in Figure 5.2a. SWNTs used in this work were grown by chemical vapor deposition (CVD) of ethanol on a highly doped silicon wafer with a ~300 nm SiO<sub>2</sub> layer, catalyzed by a Co thin film deposited onto the Si/SiO<sub>2</sub> substrate by evaporation.<sup>5,26</sup> Well-separated ultra long nanotubes can be produced by this method. A 1 mm wide stripe of gold thin film was deposited onto the SiO<sub>2</sub> surface to act as the top ground electrode. The heavily-



doped Si wafer was used as the back gate electrode. The gate voltage was provided by a Keithley 238 electrometer. Individual tubes in contact with the top gold electrode were imaged by the home-built laser-scanning confocal Raman microscope. Raman spectra of imaged SWNTs were recorded by a liquid nitrogen-cooled CCD camera attached to a spectrograph, with a typical exposure time of 2 min. The 633nm excitation laser power was kept  $< 1.0$  mW during the spectral measurement to avoid the effect of laser-heating. The resolution of the spectrometer is about  $2\text{ cm}^{-1}$ . The spectral line width reported below was not corrected for the instrumental broadening.

### 5.2.2. G band Raman spectra of metallic tubes at different voltage

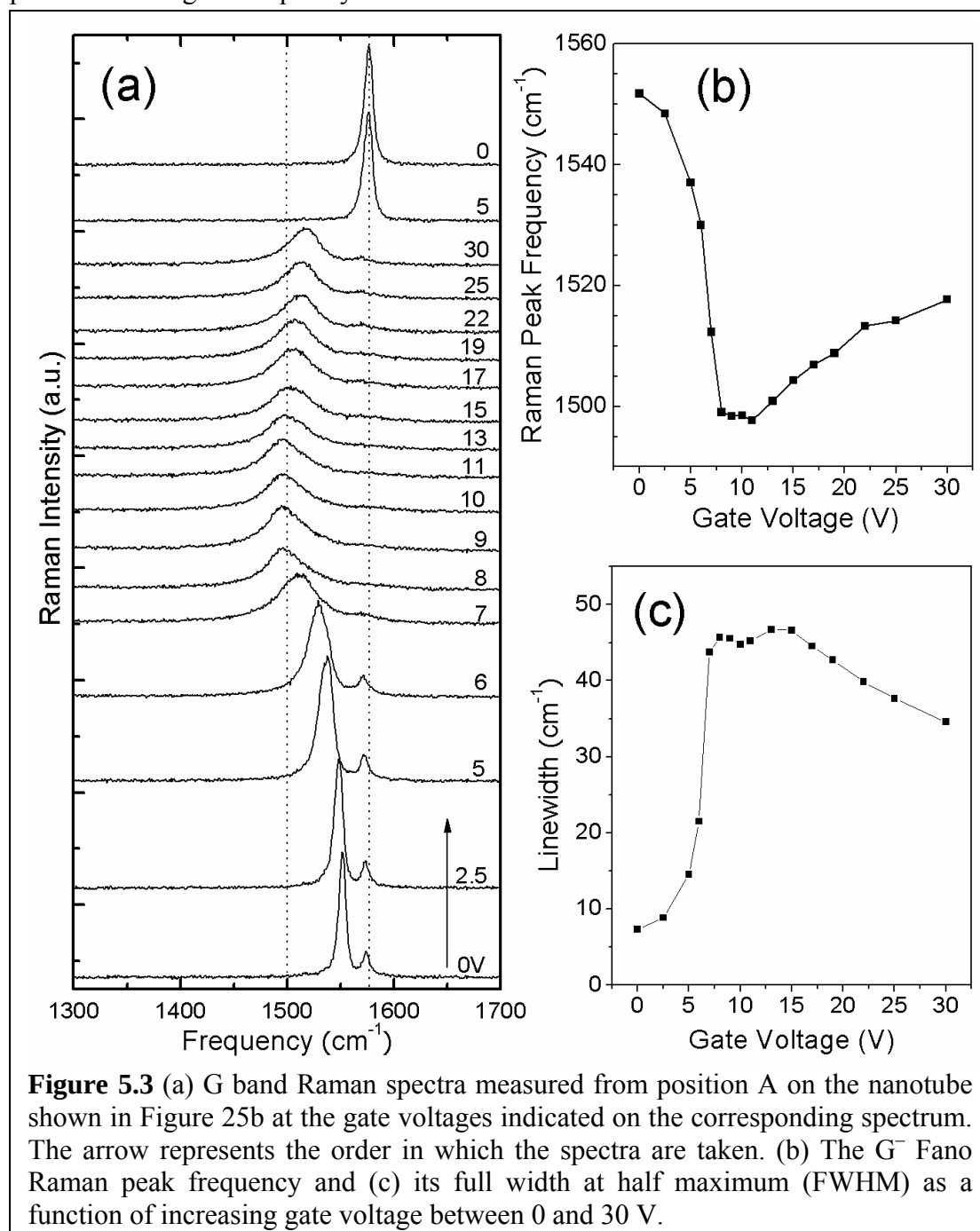
Raman imaging and spectra can be obtained on those individual nanotubes that satisfy the resonance condition with the 633nm excitation light. Figure 5.2b is a representative Raman image of a nanotube (or a thin bundle) in contact with the gold electrode. This tube has an very strong RBM of  $\sim 209\text{ cm}^{-1}$  measured at spot A around

the bent tube segment, and  $\sim 205 \text{ cm}^{-1}$  at spots along the straight segment such as B shown in Figure 5.2b. This tube is assigned to (10, 7), a metallic tube, on the basis of the RBM frequency and its intensity at spot B. The slightly higher RBM frequency at spot A presumably arises from torsional strain present in the bent segment,<sup>98,99</sup> which is probably unintentionally induced during sample handling. As will be shown below, the G band Raman spectrum from A is also influenced by the strain, consistent with the recent reports of strain effects on Raman spectra of individual SWNTs.<sup>98,99</sup>

For the metallic tube shown in Figure 5.2b, Raman spectra are first recorded from spot A as a function of gate voltage. Figure 5.3a shows the evolution of the G band Raman spectra from spot A as the gate voltage  $V_g$  is increased from 0 V to 30 V. The disorder-induced D band feature remains very weak at all  $V_g$ . In agreement with the previous reports,<sup>86,91-93</sup> the G band spectrum of this metallic tube changes dramatically with increasing gate voltage  $V_g$ . Two peaks are resolved in the G band spectra for the whole range of increasing  $V_g$  from 0 V to 30 V. The intense lower-frequency  $G^-$  peak is fitted with a BWF line, and the weak higher-frequency  $G^+$  peak is fitted by a Lorentzian line. The fitted  $G^-$  BWF peak frequency and line width (FWHM,  $2\Gamma$ ) at different  $V_g$  are summarized in Figure 5.3b and 5.3c respectively.

In the beginning, at  $V_g = 0 \text{ V}$ , the tube exhibits two sharp Raman lines at  $1552 \text{ cm}^{-1}$  ( $G^-$ , FWHM  $7.3 \text{ cm}^{-1}$ ) and  $1574 \text{ cm}^{-1}$  ( $G^+$ , FWHM  $7.7 \text{ cm}^{-1}$ ) respectively. When  $V_g$  is increased, the  $G^-$  peak gradually shifts to lower frequency and becomes increasingly broader. At  $V_g$  around 8 V, the  $G^-$  peak frequency reaches a minimum of  $\sim 1500 \text{ cm}^{-1}$  with an FWHM  $\sim 45 \text{ cm}^{-1}$ . The  $G^-$  peak slightly narrows and slowly shifts back to higher frequency when  $V_g$  is varied from 15 V to 30 V. On the other hand, the  $G^+$  peak downshifts by only  $\sim 3 \text{ cm}^{-1}$  when  $V_g$  is varied from 0 V to 7 V, at the same time it also becomes broader and weakens significantly. The  $G^+$  peak partly resumes

at  $\sim 1570 \text{ cm}^{-1}$  when  $V_g$  is increased to 22 V, coincident with the upshift of the  $G^-$  peak back to higher frequency.



As in the typical G band Raman spectra of metallic tubes, the weak higher-frequency  $G^+$  Raman component in Figure 5.3a is assigned to the transverse optical (TO) mode with C-C vibration perpendicular to the tube axis, while the intense  $G^-$  component (BWF peak) corresponds to the longitudinal optical (LO) mode in which C-C vibration is parallel to the tube axis.<sup>100,101</sup> This is opposite to the assignment in

semiconducting tubes, due to the presence of a Kohn anomaly (KA) in metallic tubes which softens the LO mode Raman frequency relative to the TO mode. Since KA originates from the coupling of the LO phonon with electrons close to the Fermi point, the LO mode frequency and line width in a metallic tube are expected to depend on the position of the Fermi level  $\varepsilon_F$  of the tube,<sup>87,92,101,102</sup> which has been observed experimentally in a number of single tube Raman studies.<sup>86,91-93</sup> It has been predicted that when  $\varepsilon_F$  is moved away from the band-crossing point between the first pair of van Hove singularities (vHSs), the LO mode gradually downshifts and its line width slightly decreases. The LO mode can reach a minimum frequency when  $|\varepsilon_F| \approx 1/2\hbar\omega_G$ , where  $\omega_G$  is the phonon frequency, followed by a pronounced upshift and line narrowing for  $|\varepsilon_F| \geq 1/2\hbar\omega_G$ . The observation in Figure 5.3 is consistent with the electron-phonon interaction mechanism. Figure 5.3 shows that the LO ( $G^-$ ) mode of the tube exhibits a minimum frequency of  $\sim 1500 \text{ cm}^{-1}$  for  $V_g$  between 7 V and 13 V, and its line width reaches nearly maximum for the same range of  $V_g$ . The Fermi level of the metallic tube is thus believed to be at the band crossing point for gate voltage  $V_{g0} \sim 10 \text{ V}$ . Initially at  $V_g = 0 \text{ V}$  the tube exhibits a narrow LO ( $G^-$ ) line at a much higher frequency of  $\sim 1552 \text{ cm}^{-1}$ . This is consistent with the fact that SWNTs are often *p*-type doped when they are stored in ambient air, and indicates  $\varepsilon_F < -1/2\hbar\omega_G$  from the band crossing point. The application of a positive gate voltage moves up the Fermi level. When  $V_g$  is increased to more than 13 V, the LO ( $G^-$ ) line becomes narrower again and also upshifts, implying that the Fermi level of the tube is now  $> 1/2\hbar\omega_G$ . Note that the rate of change in the Raman spectra is smaller for increasing  $V_g$  from 15 V to 30 V ( $V_g > V_{g0}$ ) compared with that for increasing  $V_g$  from 0 V to 10 V ( $V_g < V_{g0}$ ), probably due to the presence of trapped negative charges on the  $\text{SiO}_2$  surface and

adsorbed water molecules in proximity to the nanotube, which can screen the applied gate potential.<sup>92,97</sup>

### 5.2.3. Hysteresis behavior and irreversible behavior

Beside the spectra change, we also observed a hysteresis behavior in the G band Raman spectrum of the metallic tube under electrostatic doping in air. Figure 5.4a displays the G band Raman spectra recorded at a different position (spot B as indicated in Figure 5.2b) along the same tube after carrying out the measurement on spot A. The initial 0 V spectrum appears like the typical spectrum of semiconducting tubes, with the intense peak being at higher frequency than the weak one. The intense peak shifts greatly as a function of applied voltage  $V_g$ , while the weaker feature remains nearly at the same frequency  $\sim 1569 \text{ cm}^{-1}$  for the whole range of applied  $V_g$ . Recent calculations have predicted that the LO mode of an armchair metallic tube exhibits a dramatic shift with the position of the Fermi level while the TO mode does not show this dependence.<sup>87,92,101,102</sup> We thus assign the intense peak to the LO mode and the weaker peak to the TO mode, considering that this tube, assigned to (10, 7), is close to armchair chirality. This assignment is also consistent with that of the spectra from spot A. The spectra are fitted with a BWF line for the LO peak and a Lorentzian line for the TO peak respectively. Some examples of curve fitting are shown in Figure 5.5. Both the fitted LO and TO mode frequencies are shown in Figure 5.4b as a function of  $V_g$ . The fitted width (FWHM,  $2\Gamma$ ) and  $1/q$  asymmetry parameter for the LO mode are shown in Figure 5.4c and d, respectively. An advancing hysteresis in the gate voltage dependent Raman spectra is clearly observed in Figure 5.4b-d in terms of the LO mode frequency, line width, and  $1/q$ . The LO mode frequency appears higher at a decreasing  $V_g$  than at the same but increasing  $V_g$ , while the opposite is observed in

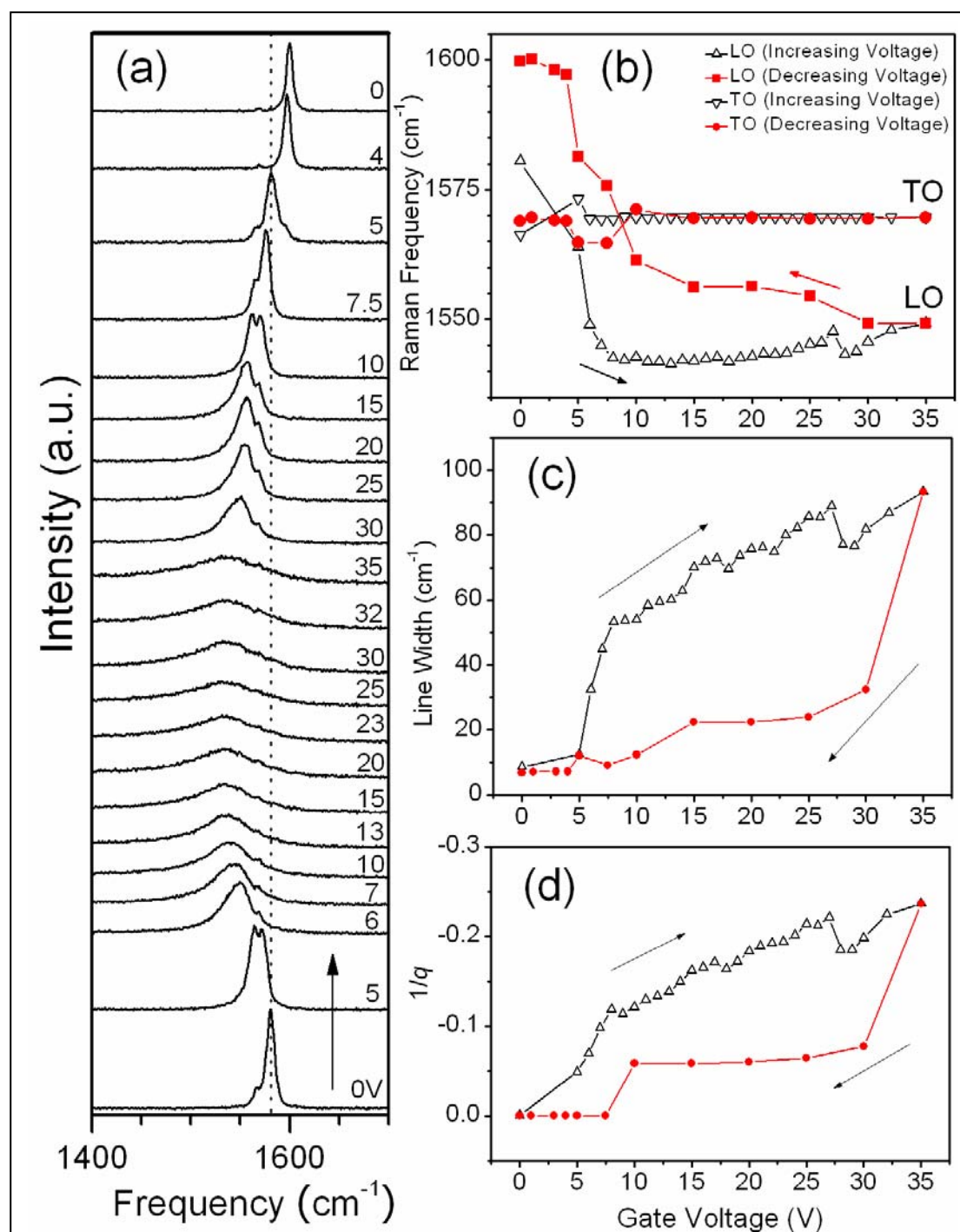


**Figure 5.4** (a) G band Raman spectra measured from position B on the nanotube shown in Figure 25b, at different gate voltages indicated on the corresponding spectrum. The arrow represents the order in which the spectra are taken. (b) LO mode and TO mode frequency, (c) LO mode full width at half maximum (FWHM) and (d) LO mode asymmetry parameter  $1/q$ , as a function of gate voltage increasing from 0 to 35 V (open symbols) and decreasing from 35 V back to 0 V (filled symbols). The arrows in b-d indicate the voltage sweeping direction.

the case of the LO mode line width and  $|1/q|$ . The initial spectrum at 0 V is reproduced as  $V_g$  is decreased to  $\sim 5$ -7 V. When  $V_g$  is decreased to 0 V, the intense LO

mode is seen to further upshift to  $\sim 1600 \text{ cm}^{-1}$ , which is much higher than the original 0 V LO mode frequency. It indicates more  $p$ -type doping in the tube now than initially at  $V_g = 0 \text{ V}$ . This advancing hysteresis in the Raman spectra is analogous to the hysteresis commonly observed in the electrical transport characteristics of semiconducting tubes stored in air,<sup>95-97</sup> and can be ascribed to a mechanism involving negative charge trapping from the tube to the  $\text{SiO}_2$  layer in the presence of a high gate voltage.

The doping induced Raman spectral change of the metallic tube, which was stored in air, also exhibits an irreversible behavior. As seen in Figure 5.3a for spectra measured from spot A, when  $V_g$  is changed from 30 V directly back to 0 V, the resulting Raman spectrum is different from the initial spectrum at 0 V. The new spectrum shows a single peak at  $\sim 1576 \text{ cm}^{-1}$ , upshifting by  $\sim 14 \text{ cm}^{-1}$  from the intense  $G^-$  peak in the initial spectrum but positioned close to the initial weak  $G^+$  peak at  $1574 \text{ cm}^{-1}$ . This single Raman feature in the new spectrum is probably a superposition of the shifted  $G^-$  peak and the relatively stable  $G^+$  peak. When  $V_g$  is increased again to 20 V, the sharp G band Raman spectrum does not exhibit significant changes any more. A similar irreversible behavior is also observed for spectra from spot B. This irreversible behavior seems to arise from the probable damage of the tube caused by laser heating and the presence of high gate voltage. However, the disorder-induced D band Raman feature remains very weak and does not exhibit any increase in intensity for all  $V_g$ . Raman measurements on a second metallic tube, which has undergone two cycles of positive gate voltage sweeping without laser illumination, also reveal a sharp G band spectrum which is nearly independent of the gate voltage. Thus the irreversible behavior is mainly caused by the influence of the gate voltage. The mechanism for the gate hysteresis can also explain the irreversible behavior of the

Raman spectra, which involves the trapping of negative charges on SiO<sub>2</sub> surface around the nanotube that is induced by the high positive gate voltage and possibly assisted and stabilized by water adsorbates. Due to the accumulated long holding time (~1 hr) of the positive gate voltage, the decay of the trapped negative charges from SiO<sub>2</sub> surface back to the tube may be slow.<sup>95,97</sup> When the gate voltage is decreased to 0 V, the tube is thus more *p*-type doped, resulting in a sharp G band spectrum. The trapped negative charges can act to screen the gate potential,<sup>95</sup> leading to the nearly absence of gate dependence of the Raman spectrum after the initial 1-2 cycles of gate voltage sweeping. Since the irreversible behavior was not observed for similar measurements in vacuum, water adsorbates and possibly O<sub>2</sub> must play important roles in the trapping and stabilizing of negative charges. It is observed that the broad BWF peak recovers in the metallic tubes after annealing the sample at 200 °C in H<sub>2</sub> for 1 hr.

#### 5.2.4. LO-TO phonon interaction

Raman spectra measured from spot B also allow us to examine the gradual evolution of the LO peak relative to the TO peak as  $V_g$  is varied. In Figure 5.4a, the initial spectrum at 0 V looks like a typical spectrum of semiconducting tubes, with the intense LO mode having a higher frequency than the TO mode. When  $V_g$  is initially increased from 0 to 6 V, the intense LO mode downshifts to a position lower than the TO mode frequency. When  $V_g$  is decreased from 10 V to 7.5 V after sweeping to 35 V, the LO mode is observed to upshift across the TO mode from lower frequency back to higher frequency. The two crossings of the LO mode over the TO mode occur at different  $V_g$  because of the gate hysteresis discussed above. Raman spectra at different increasing  $V_g$  around the first crossing are replotted in Figure 5.5 together with curve fittings to highlight the spectral evolution. The assignment of LO and TO modes is

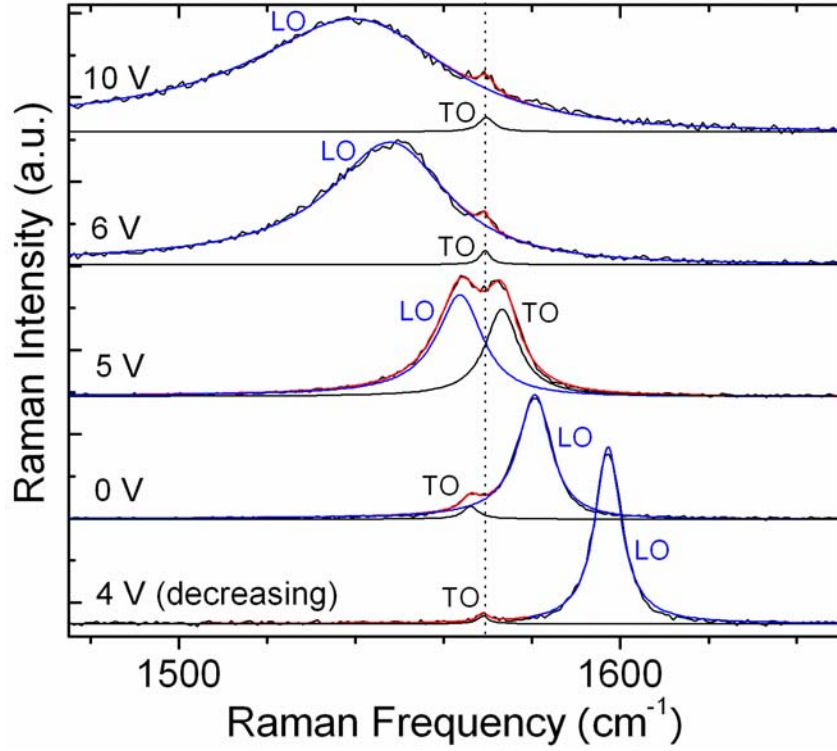


**Figure 5.5** G band Raman spectra from position B on the studied nanotube at the increasing gate voltage of 0 V, 5 V, 6 V, and 10 V, and at decreasing gate voltage of 4 V. From bottom to top the G band spectrum gradually evolves from a sharp semiconducting type spectrum to the typical broad BWF type spectrum as the degree of *p*-type doping of the tube decreases. The spectra are fitted with a BWF line (blue curve) for the LO peak and a Lorentzian line (black curve) for the TO peak, respectively. Red curves are the fitted spectra.

indicated in Figure 5.5. The spectrum for decreasing  $V_g = 4$  V is also plotted, at which the tube is more *p*-doped than at initial 0 V because of the gate hysteresis. The spectra in Figure 5.5 from bottom to top thus correspond to Fermi level of the tube being moved up toward the band crossing point, with the LO mode gradually downshifting and broadening. At  $V_g = 4$  V (decreasing), 6 V, and 10 V, the weak TO mode of the tube is located at a stable frequency of  $\sim 1569$   $\text{cm}^{-1}$ . The spectrum at increasing  $V_g = 5$  V (also at decreasing  $V_g = 10$  V) exhibits a very different behavior. In contrast to the much lower intensity of the TO mode relative to the LO mode at other  $V_g$ , both peaks in the 5 V spectrum exhibit comparable intensity. The stable TO mode frequency of  $1569$   $\text{cm}^{-1}$  observed at other  $V_g$  interestingly lies in between the two peaks in the 5 V spectrum. We assign the lower-frequency peak in the 5 V spectrum to the LO mode

and the higher-frequency peak to the TO mode, on the basis of the mode assignment in the spectrum at the nearest gate  $V_g = 6$  V. Thus at  $V_g = 5$  V, the LO mode has just downshifted across the TO mode, which is observed to have a frequency higher than the stable value of  $1569\text{ cm}^{-1}$ . On the other hand, at 0 V the LO mode is still located above the TO mode, and it can be seen that the TO mode frequency is slightly lower than the stable  $1569\text{ cm}^{-1}$ . These observations suggest evidence of an “anti-crossing” type phonon interaction between these two modes when they are degenerate, as proposed in an early study by Maultzsch and coworkers.<sup>103</sup> Recent calculation has predicted that a phonon mixing between LO and TO modes is absent due to the time-reversal symmetry.<sup>87</sup> The breaking of this symmetry possibly occurs in Raman scattering from position B on the tube. This is an interesting issue for further study.

### 5.2.5. Torsional strain in the bend SWNTs

It is noted that the LO ( $G^-$ ) mode minimum frequency of  $\sim 1500\text{ cm}^{-1}$  at spot A for  $\varepsilon_F \approx 0$  appears much lower than the corresponding frequency at spot B and also the previously reported values of  $\sim 1550\text{ cm}^{-1}$  for individual metallic tubes of similar diameters.<sup>86,91-93</sup> Laser heating effect can be ruled out since the low laser power adopted ( $\sim 1$  mW) is unlikely to cause a Raman frequency downshift of such a magnitude. We tentatively attribute this large downshift to the effect of torsional strain present in the bent tube segment around spot A, as it has been reported that the BWF peak of a metallic tube under torsional strain can downshift by as much as  $\sim 50\text{ cm}^{-1}$ .<sup>98,99</sup> Under torsional strain the RBM of a SWNT was also shown to exhibit a slight upshift.<sup>98,99</sup> Our observation of a slight higher RBM at spot A compared to spot B is consistent with the presence of torsional strain in the bent tube segment around spot A. The observed gate dependence of Raman spectra from spot A suggests that

the electron-phonon interaction is still present in a bent metallic tube. In addition, Figure 5.4 shows a different gate dependence of the Raman spectra from point B compared to that measured on spot A shown in Figure 5.3. This difference is attributed to the heterogeneous distribution of local charge traps surrounding the nanotube and also the influence of torsional strain present in the bent tube.

We also note the large magnitude of the change in the  $G^-$  BWF peak position and line width as  $V_g$  is varied in the present work. Tsang and coworkers reported a reversible change in the G band Raman spectrum of a metallic tube with a similar sample structure but placed in vacuum, as a function of  $V_g$ .<sup>92</sup> Although the range of  $V_g$  was similar to the present work, the observed change in the BWF peak frequency and line width was only  $\sim 12 \text{ cm}^{-1}$  and  $20 \text{ cm}^{-1}$  respectively, much smaller than the corresponding values of  $50 \text{ cm}^{-1}$  and  $80 \text{ cm}^{-1}$  observed on the tube exposed to ambient air shown in Figure 5.4. On the other hand, our values of the shift in BWF peak frequency and line width are close to those obtained with efficient polymer electrolyte gating.<sup>86,93</sup>

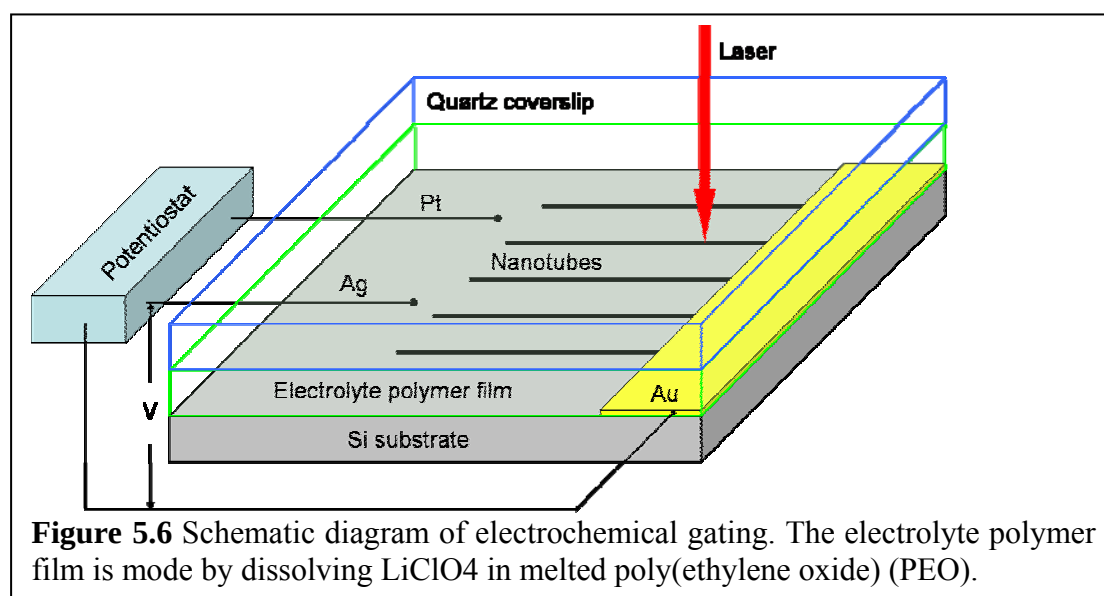
### 5.3. Electrochemical doping

In previous section, the electrostatic gating is applied to study the electron-phonon interaction of metallic nanotubes. However, as shown above, this method has a big flaw in that the change of Raman spectra with the gate voltage is irreversible, most likely due to the trapping of negative charges assisted by  $O_2$  and water from air. Therefore the electrochemical gating method was developed to solve this problem. In electrochemical gating, a voltage is applied between a nanotube and a reference electrode in an electrolyte solution. According to the literature, electrochemical gating is a more efficient and reversible way to change the doping level of nanotubes.

In this experiment, we used the electrochemical doping method to apply both negative and positive charges on several nanotubes, including both metallic and semiconducting tubes. The doping-induced Raman spectral changes of metallic and semiconducting tubes are measured. Preliminary results indicate that electrochemical gating is reversible, and Raman spectra change agrees well with early observation from electrostatic doping experiment.

### 5.3.1. Experimental section

The schematic diagram of the sample used for electrochemical gating in this work is shown in Figure 5.6. SWNTs were grown by chemical vapor deposition (CVD) of ethanol on a highly doped silicon wafer with a  $\sim 300$  nm  $\text{SiO}_2$  layer. The catalyst is Co thin film deposited onto the Si/ $\text{SiO}_2$  substrate by evaporation. Same as in the electrostatic doping experiment, a 1 mm wide stripe of gold thin film with thickness  $\sim 80$  nm was deposited onto the  $\text{SiO}_2$  surface. Then a thin layer of electrolyte polymer film, which is made by dissolving electrolyte  $\text{LiClO}_4$  in viscous oligomer poly(ethylene oxide) (PEO), was added onto the surface of the sample. At last a quartz coverslip was placed on the top of the film to hold everything, and most



importantly, to provide a flat surface and facilitate Raman imaging. The 633 nm excitation laser was focused on the isolated nanotubes through the coverslip and the electrolyte polymer film.

In this experiment, instead of using a normal two-electrode system, we used a three electrode electrostat system. A silver wire is used as the reference electrode, a platinum wire as the counter electrode, and the gold thin film/nanotubes as the working electrode. The voltage applied between the Au working electrode and the Ag reference electrode is controlled by a potentiostat (BAS CV-1B). Simultaneously the electrochemical current is monitored by the same potentiostat

Due to the strong Raman scattering of the electrolyte polymer around 1470  $\text{cm}^{-1}$ , the background of Raman images taken through the electrolyte polymer film is higher than the Raman images in air (Figure 5.7). However, according to the images in Figure 5.7, we still are able to identify the same tubes at the two conditions.

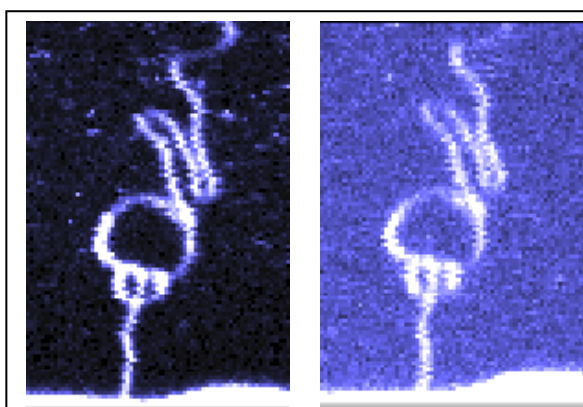


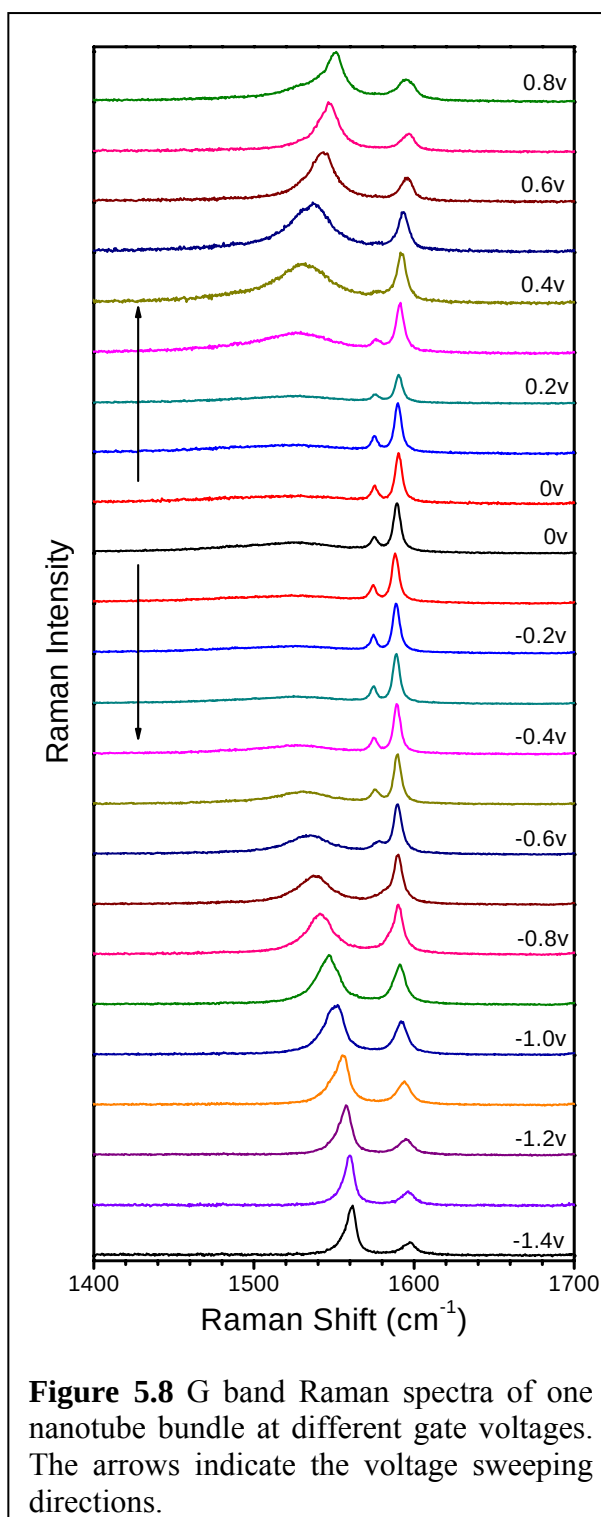
**Figure 5.7** The Raman images of one nanotube in the air (left) and through the electrolyte polymer film (right). The bright part in the bottom is the gold thin layer.

### 5.3.2. Raman spectra at different voltages

In this experiment, we applied both positive and negative voltages to tune the Fermi level of metallic and semiconducting nanotubes. The doping induced Raman spectral change was observed in these tubes. Figure 5.8 shows the G band Raman spectral change of a small nanotube bundle. This nanotube bundle, which has two RBM peaks at  $\sim 147$  and  $\sim 220 \text{ cm}^{-1}$ , is suspected to consist of one metallic nanotube

and one semiconducting tube, as also seen from its G band spectra. It is difficult to assign the  $\sim 147\text{ cm}^{-1}$  semiconducting tube, due to the large number of possible tubes around this range. The metallic tube with intense RBM peak whose frequency  $\sim 220\text{ cm}^{-1}$  is tentative assigned to (13, 1).

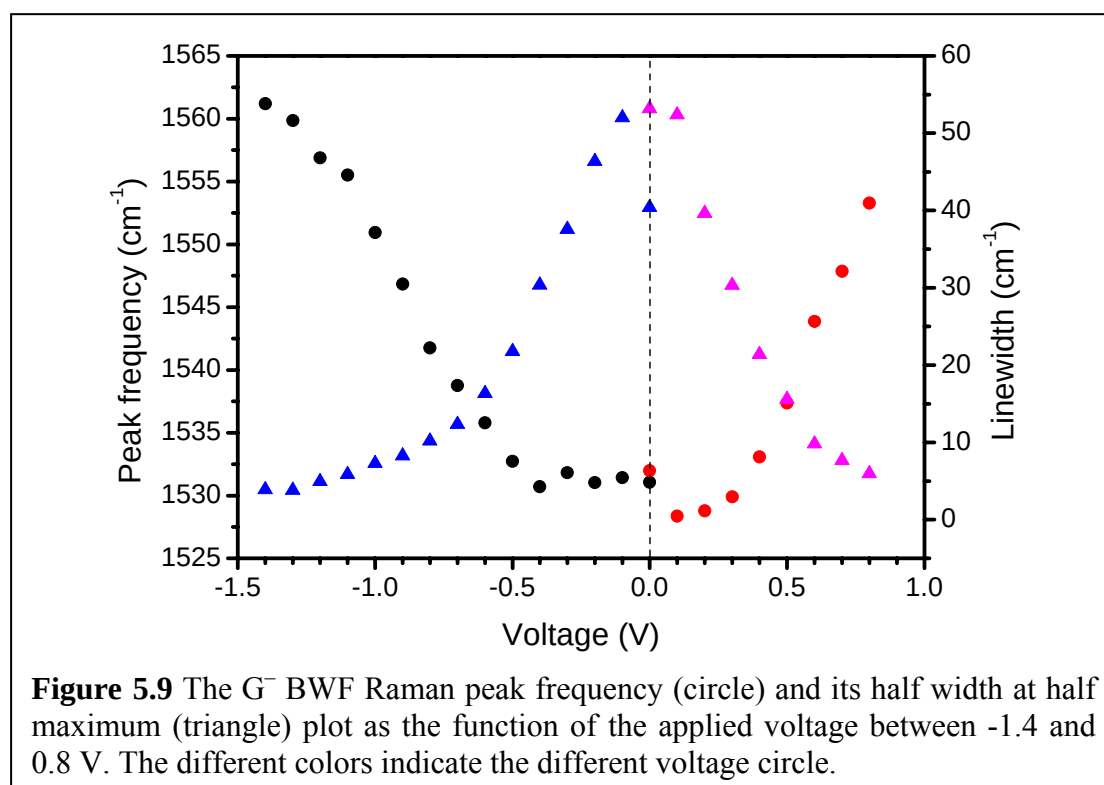
For the nanotube bundle in Figure 5.8, we first applied negative voltage from 0 to -1.4 V by a step size of 0.1 V, and then slowly changed the voltage back to 0 V. After that the positive voltage is applied to the tubes by same step until 0.8 V. By looking at the spectra, we make the following two observations. First when the voltage went back to 0 V from the -1.4 V, the spectrum is almost same as the



beginning spectrum at 0 V, which indicates that the electrochemical doping process is reversible, unlike the electrostatic doping. During the measurement, after several voltage sweeping cycles, we are still able to observe the broad G band peak of metallic tubes. Second, in our electrostatic doping experiment, we need tens of volts

to induce significant changes to Raman spectra. On the contrary, in electrochemical gating only  $\sim 1$  V is necessary to make the same magnitude of spectral change, which proved the electrochemical doping is a more efficient way to charge nanotubes.

In Figure 5.8, the lowest-frequency G band peak is assigned to the  $G^-$  peak (LO) of the (13, 1) metallic tube due to its BWF line shape and its significant change

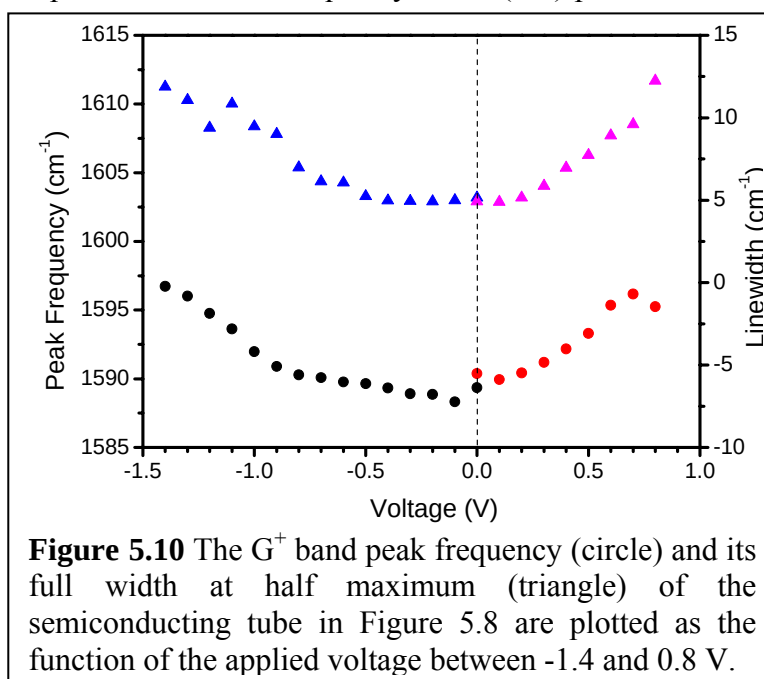


when the voltage is applied. The fitted BWF peak frequency and line width (HWHM,  $\Gamma$ ) at different voltages are plotted in Figure 5.9. At 0 V, the BWF peak seems to have largest line width and its G band Raman frequency is around  $1531 \text{ cm}^{-1}$ . When the voltage is increased or decreased away from 0 V, the  $G^-$  peak slowly moves to higher frequency and its line width gradually decreases, which is more consistent with the calculation results than the early electrostatic doping result is. In this case, the zero doping level of the tube is around 0 V, suggesting this metallic tube was not doped by the solvent. Further the  $G^-$  peak frequency in Figure 5.9 even exhibits two minima, located at -0.4 and 0.1 V respectively, which should correspond to the Fermi level positions of  $\pm 1/2 \hbar \omega_G$ .

In Figure 5.9, the maximum frequency change is  $\sim 30 \text{ cm}^{-1}$ , which is smaller than the data from electrostatic doping experiment. Also the G band spectra at high-doping level in this experiment do not show same semiconducting-type line shape as in previous electrostatic experiment. The reason for this is that the applied voltage, limited by the electrochemical stability of the electrolyte solution, is not enough to reach same doping level as before. We observed that when the voltage is over  $-1.4 \text{ V}$  and  $0.8 \text{ V}$ , the current increased dramatically, indicating the onset of some electrochemical reactions in the solution.

In Figure 5.8, besides the BWF peak, there are additional two Lorentzian peaks. The strong peak at highest frequency is tentatively assigned to be the  $G^+$  (LO mode) peak of the semiconducting tube. The weak Lorentzian peak at lower frequency, located between the  $G^-$  band of the metallic tube and the  $G^+$  peak of the semiconducting tube, is difficult to determine whether it belongs to the metallic tube or semiconducting tube. It is tentatively assigned to the TO mode of semiconducting tube. Since the electron-phonon interaction mostly affects the LO phonon, here we only focus on the assignable  $G^+$  peak. The Raman frequency of  $G^+$  (LO) peak and its

line width (FWHM) are plotted as a function of applied voltage in Figure 5.10. From the figure, we can see that LO mode of the semiconducting tube also exhibit a doping dependence. This behavior is also observed on another



individual semiconducting nanotube. For semiconducting tubes, the change of  $G^+$  band peak frequency is  $\sim 10\text{ cm}^{-1}$ , which is much smaller than the spectral change of metallic tube,  $\sim 30\text{ cm}^{-1}$  at same voltage range. The line width for semiconducting tube increases when the doping level moves away from band-crossing point, which is opposite to the behavior of metallic tubes. Understanding of the mechanism of doping dependence in semiconducting tubes requires more further study.

### 5.3.3. Electrochemical reactions

As shown above, the electrochemical doping process is reversible and can be repeated in many voltage circles. However, in our experiment, we encountered big problem. If we apply too big voltage (larger than 1.4 V) or leave the sample in the air for more than two days, the Raman signal of nanotube will become 100 times stronger than the original Raman signal, which suggests a huge enhancement effect. Figure 5.11 shows a high resolution microscope image of one sample after the electrolyte

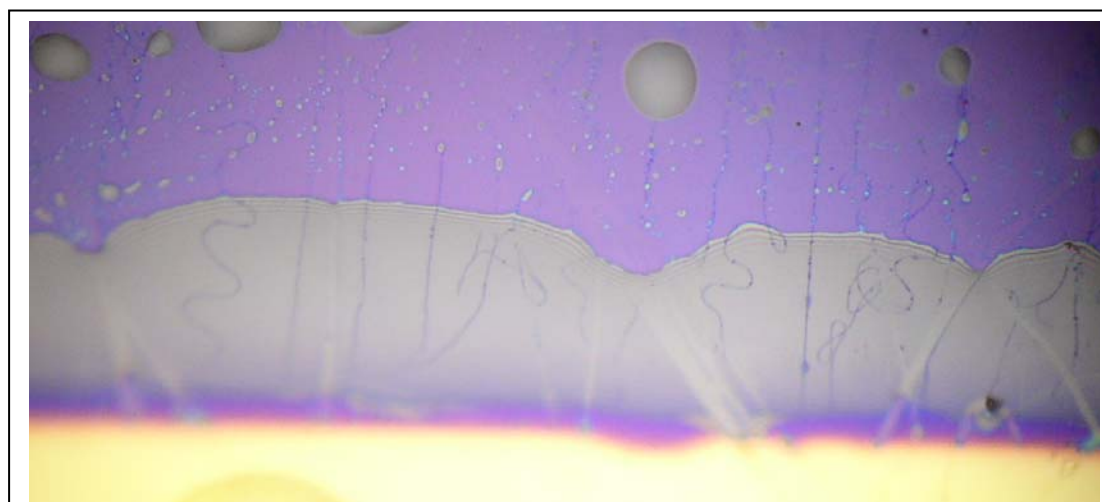


**Figure 5.11** A high resolution microscope image of one nanotube sample after removing the electrolyte polymer film. The yellow part on the bottom is the gold thin layer, and the grey part is remained polymer solution.

polymer solution is removed. Close inspection reveals that small black particles have appeared along most nanotubes, which make nanotubes visible under an optical microscope. We suspect that some electrochemical reactions between the electrodes

have happened at high voltage, which formed silver or gold nanoparticles along nanotubes. These metal nanoparticles will cause surface enhancement to the Raman signal of nanotubes. Also it was suspected that  $O_2$  and water from the air or the polymer solution helped the occurring of these electrochemical reactions.

In order to solve this problem, the future work will find more stable electrolyte solution and electrode which can work in higher voltage. Another way to improve the experiment is to put sample in nitrogen during the experiment, which can avoid the sample from  $O_2$  and water in the air.

#### **5.4. Summary and future direction**

We have observed significant irreversible changes in the G band Raman spectrum of a metallic nanotube exposed to ambient air under electrostatic gating. The gate dependent LO mode shift and broadening of this near-armchair tube exhibit a much larger magnitude as well as a significant hysteresis behavior compared to the previous similar Raman scattering studies of nanotubes placed in vacuum.<sup>92</sup> we attribute these behaviors to the trapping of negative charges on  $SiO_2$  around the nanotube,<sup>82,95,96</sup> which is believed to be assisted and stabilized by water adsorbates. It is interesting to see that the typical semiconducting type G band Raman spectra, in which the LO mode is in higher frequency than the TO mode, are resolved when the metallic tube is highly doped. Such a metallic tube also allows us to observe the smooth gradual evolution of the G band spectrum from semiconducting type to the typical broad BWF type, which provides preliminary evidence of phonon interactions between LO mode and TO mode when having same frequency.

We also observed the reversible changes in the G band Raman spectrum of a few metallic and semiconducting tubes inside the electrolyte polymer solution by

electrochemical gating, which proves to be a more efficient way than electrostatic gating. The G band spectra change of metallic nanotubes is almost consistent with the previous data. However the electrochemical reaction between the electrolyte solution and metal electrode wire affect the Raman spectra at high voltage, which needs to be solved in the future work.

Also as I mention before, the change of the G band Raman spectra with different doping level has temperature dependence. At low temperature, the line width is expected to change more steeply and the two minima of the Raman frequency will be more observable. Therefore the low temperature study of charge doping of metallic SWNTs will be very interesting.

## Chapter 6

### Temperature dependence of Raman spectra of SWNTs and single-layer graphene

The Raman spectra of SWNT bundles<sup>16,104-108</sup> and single-layer graphene (SLG)<sup>109-111</sup> at different temperatures, including cryogenic temperature measurements,<sup>110,112-115</sup> have been investigated previously in an attempt to obtain more resolved structural information and to understand the atomic bond structure and thermal properties of SWNTs and graphene. The temperature dependence of Raman frequencies of a material is in general due to the anharmonic terms in the bond potential energy. The early studies on the temperature dependent Raman scattering in SWNTs were carried out on SWNT bundles, giving rise to inhomogeneously broadened Raman spectra due to the presence of many tubes with different  $(n, m)$  chiral structure. Since the optical transition energies  $E_{ii}$  of nanotubes depend on temperature,<sup>116-120</sup> it is possible that different  $(n, m)$  structured tubes present in a bundled sample could be selected by resonant Raman scattering at different temperatures. This can result in an apparent change in the Raman spectra and can complicate the measurement of intrinsic, temperature-induced Raman spectral change in SWNTs. In addition, tube-tube interaction in bundled nanotubes can also influence the temperature dependence of Raman spectra of SWNTs.<sup>106</sup> Because a SWNT can be viewed as a wrapped seamless graphene sheet, it should also be interesting to compare the temperature dependence of Raman scattering from these two closely related materials.<sup>109</sup>

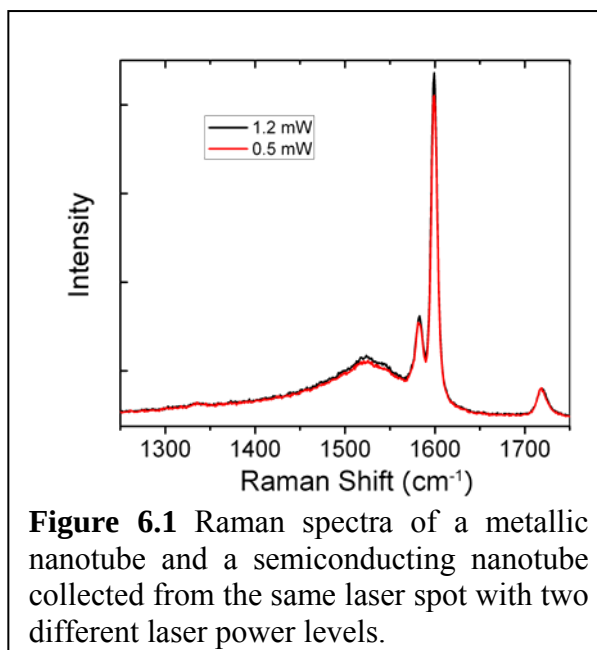
In this chapter, I will show the work in which confocal Raman microscopy is used to record the Raman spectra of individual SWNTs and single-layer graphene on

silicon substrates at both room and low temperatures. We find that the change in Raman frequencies induced by temperature variation depends on the tube diameter with larger-diameter tubes and graphene showing a stronger temperature effect. Our results also provide evidence that tube chirality also affects the temperature-induced Raman frequency change of individual SWNTs. We discuss the temperature-induced Raman frequency change in SWNTs based on the bond force constant model, taking into account the tube curvature effect and tube-substrate interaction. The temperature dependence of the BWF Raman peak of metallic tubes shows a large variation among different individual tubes, which can be ascribed to different degrees of charge doping in the context of electron-phonon interaction mechanism discussed in chapter 5.

### **6.1. Experimental section**

The SWNT samples used in this work were grown by chemical vapor deposition (CVD) of ethanol on silicon wafer with a  $\sim 200$  nm SiO<sub>2</sub> layer, as described in early chapter. Single-layer graphene was prepared by the micromechanical isolation method on a silicon wafer as illustrated by Novoselov et al.<sup>121,122</sup> The beam scanning confocal microscopy has been described in chapter 2. For the low temperature experiments, the silicon wafer was mounted in vacuum on the cold plate of a continuous flow liquid helium optical cryostat (Oxford Instruments, MicrostatHiResII). The distance from the sample to the cryostat optical window is kept  $>1$  mm. The 40x dry objective, with a correction collar adjustment, focuses the laser beam through the cryostat optical window to the sample plane. The excitation wavelength used was 633 nm for SWNTs and 488 nm for graphene. Also the excitation laser power was kept  $\sim 3.0$  mW for imaging, and  $<1.0$  mW for spectral measurement to avoid the effect of laser-heating. No laser power dependence of the

Raman spectra of both metallic and semiconducting tubes was observed for power  $<1.0$  mW. (Figure 6.1) The resolution of the spectrometer is about  $2\text{ cm}^{-1}$ . The spectral line width reported below was not corrected for instrumental broadening. Raman spectroscopy of individual SWNTs was performed at room temperature



and nominal 5 K only. No attempt was made for intermediate temperatures due to the limited supply of the cryogen. The  $520\text{ cm}^{-1}$  Raman peak of the silicon substrate at room temperature was found to upshift to  $524\text{ cm}^{-1}$  when the sample was cooled to nominal 5 K, in quantitative agreement with the early observation by Hart et al.<sup>123</sup>

## 6.2. Raman spectra of SWNTs and SLG at different temperature

In this experiment, we were able to follow the same sample areas at both room temperature and low temperature. Parts a and b of Figure 6.2 show Raman images of a nanotube on Si/SiO<sub>2</sub> substrate acquired at 295 and nominal 5 K, respectively. The image area is  $50\text{ }\mu\text{m} \times 85\text{ }\mu\text{m}$ , and the integration time is 15 ms for each pixel. The irregular bright features, in particular the substrate edge in this case, were used to identify and locate the same sample area. Although the emission background increases at low temperature, the same nanotube can be clearly identified in both images. We followed seven semiconducting tubes (denoted by S1-7) and five metallic tubes (denoted by M1-5) at both 295 and 5 K in Raman imaging with 633 nm excitation, which allowed us to measure the temperature dependent Raman spectra of

individual nanotubes. Raman imaging was also performed on SLG with 488 nm excitation at various low temperatures ranging from 295 to 5 K.

The RBM and  $G^+$  peak Raman frequencies at 295 K, and their upshift when  $T$  is decreased from 295 to 5 K for these SWNTs and SLG are all listed in Table II, along with their diameter and tentative  $(n, m)$  assignment.

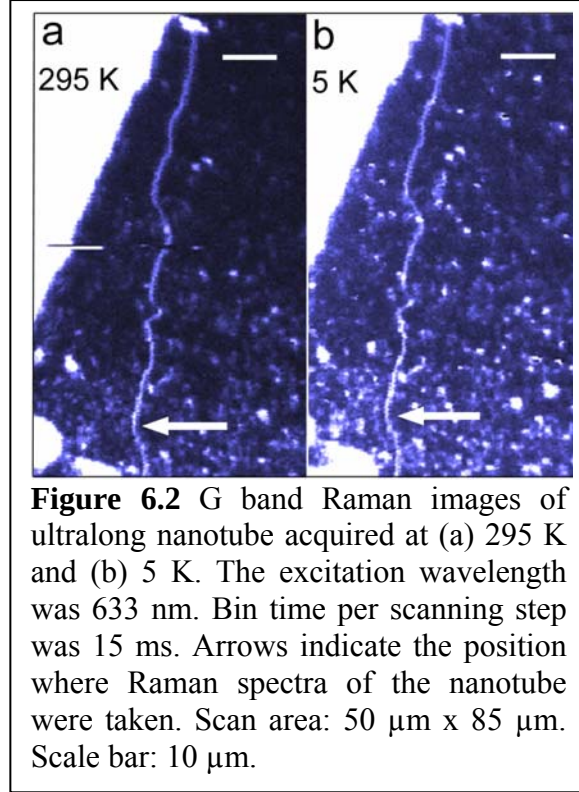


**Table II.** Measured RBM and  $G^+$  mode frequencies of individual SWNTs and SLG at 295 K, and their change when the temperature is lowered from 295 K to 5 K.

|     | RBM <sub>295K</sub><br>(cm <sup>-1</sup> ) | $G^+$ <sub>295K</sub><br>(cm <sup>-1</sup> ) | $d_t^a$<br>(nm) | $\Delta\omega_{G^+}^b$<br>(cm <sup>-1</sup> ) | $\Delta\omega_{\text{RBM}}^c$<br>(cm <sup>-1</sup> ) | $(n, m)$        |
|-----|--------------------------------------------|----------------------------------------------|-----------------|-----------------------------------------------|------------------------------------------------------|-----------------|
| S1  | 298.6                                      | 1582.8                                       | 0.78            | 1.9                                           | 0.1                                                  | (8,3)           |
| S2  | 140                                        | 1584.6                                       | 1.74            | 4.3                                           |                                                      | (15,11), (16,9) |
| S3  |                                            | 1595.0                                       | 2.02            | 4.2                                           |                                                      |                 |
| S4  |                                            | 1608.5                                       | 1.86            | 3.4                                           |                                                      |                 |
| S5  |                                            | 1588.9                                       | 0.97            | 2.6                                           |                                                      | (8,6)           |
| S6  | 227                                        | 1582.5                                       | 1.04            | 2.0                                           | 0                                                    | (12,2)          |
| S7  | 284.7                                      | 1586.1                                       | 0.83            | 3.5                                           | 0                                                    | (7,5)           |
| SLG |                                            | 1578.5                                       | $\infty$        | 6.5                                           |                                                      |                 |
| M1  | 169                                        | 1590                                         | 1.42            | 4.0                                           | 2.5                                                  | (18,0)          |
| M2  | 192                                        | 1586.9                                       | 1.24            | 1.0                                           | 2.2                                                  | (9,9)           |
| M3  | 213                                        |                                              | 1.10            |                                               | 0                                                    | (11,5)          |
| M4  | 180.9                                      | 1584                                         | 1.32            | 3.5                                           | 2                                                    | (16,1), (15,3)  |
| M5  | 173                                        | 1577.5                                       | 1.38            | 4.5                                           | 2.2                                                  | (14,5), (13,7)  |

<sup>a</sup> The tube diameter  $d_t$  is estimated using equation (6.2) for tubes showing an RBM and using equation (6.3) for tubes without showing an RBM.

<sup>b</sup>  $\Delta\omega_{G^+} = \omega_{G^+, 5K} - \omega_{G^+, 295K}$ .

<sup>c</sup>  $\Delta\omega_{\text{RBM}} = \omega_{\text{RBM}, 5K} - \omega_{\text{RBM}, 295K}$ .

### 6.2.1. Single-layer graphene

Graphene, as an ideal two-dimensional single layer of carbon atoms, has attracted much attention since its micromechanical preparation was published recently.<sup>121,122</sup> Graphene exhibits unique electronic properties such as the unusual quantum hall effect and the very high electron mobility.<sup>124-126</sup> Graphene shows two main Raman features, including the G band at  $\sim 1580\text{ cm}^{-1}$  and the 2D band (the overtone of the disorder-induced D band; also called G' band) at  $\sim 2700\text{ cm}^{-1}$ .<sup>127-129</sup> The 2D band Raman line shape can be used to identify the number of graphene layers.<sup>127,130</sup> In addition, recent Raman scattering experiments<sup>93,131,132</sup> on graphene and metallic SWNTs subjected to the application of a gate voltage revealed a very strong electron-phonon coupling in both materials, confirming the predicted Kohn anomaly (KA) in their phonon dispersion.<sup>101,102,133,134</sup>

In this experiment, temperature-dependent Raman scattering was performed on SLG with 488 nm excitation. While the graphene 2D band position is sensitive to laser excitation energy due to the double resonance Raman mechanism, its G mode frequency has been shown to be independent of the excitation energy.<sup>135</sup> Figure 6.3a shows a Raman image of an SLG acquired by detecting the 2D band Raman intensity while the laser focal spot was scanned over the sample plane at 295 K. The area enclosed by the dashed lines in the Figure 6.3a corresponds to an SLG, as also confirmed by optical microscopy observation<sup>122</sup> (image not shown). Figure 6.3c shows the G band and 2D band Raman spectra of the SLG at various temperatures between 295 and 5 K. The 2D band line shape is consistent with the Raman signature previously used to identify an SLG.<sup>127,128</sup> The G band line width ( $\sim 13\text{ cm}^{-1}$ ) for  $T = 295\text{ K}$  in Figure 6.3c is slightly smaller than the typical value of  $\sim 14\text{-}16\text{ cm}^{-1}$  for undoped graphene, and the Raman intensity ratio  $I_{2D}/I_G$  is also smaller when

compared to the intrinsic graphene.<sup>135</sup> This suggests that our graphene sample is probably weakly, unintentionally doped. At 5 K, the G band is asymmetrically broadened, indicating inhomogeneous charge doping, as suggested by Casiraghi et al.,<sup>135</sup> or due to thermally induced structural inhomogeneity at low temperature.

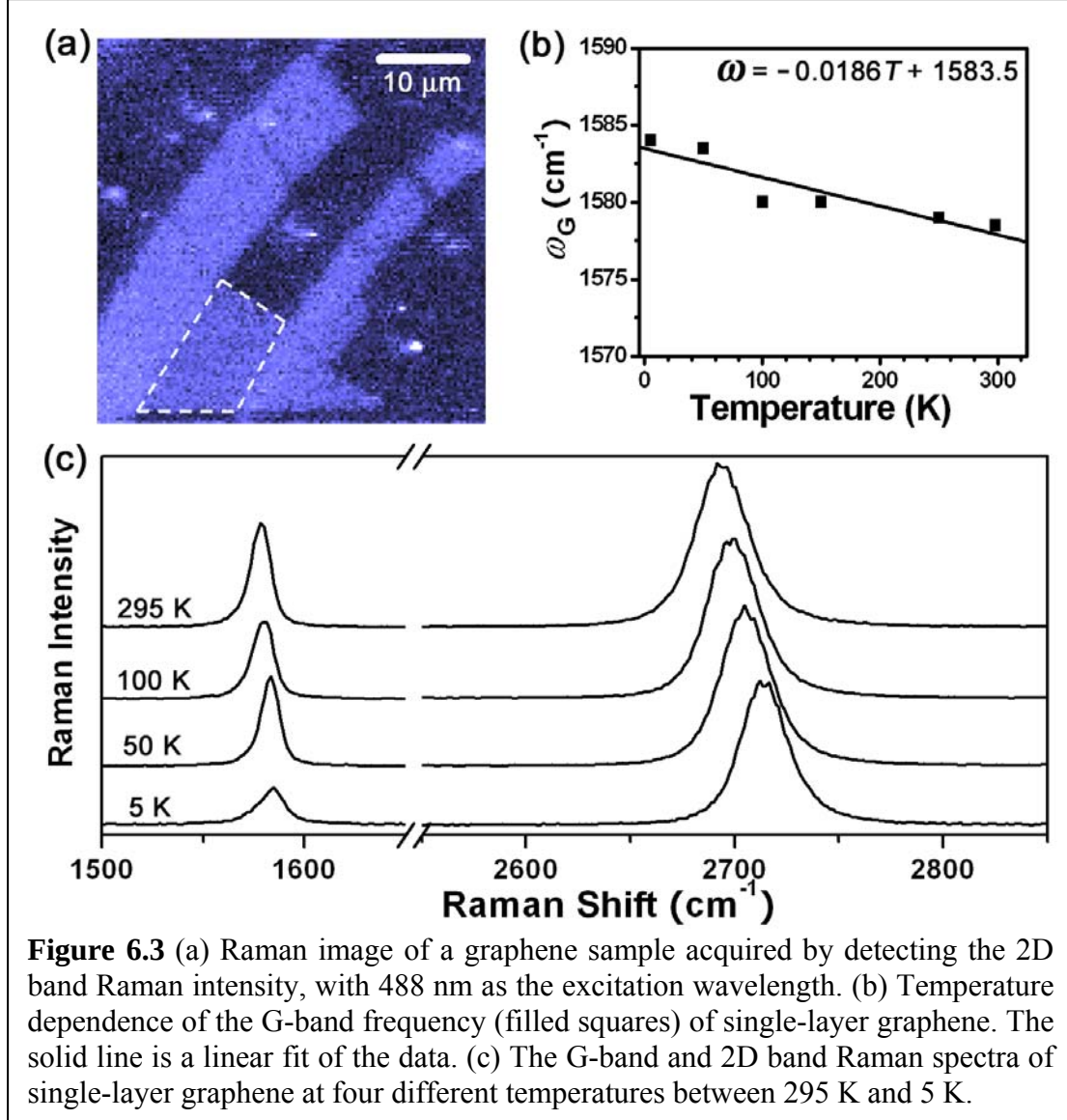


**Figure 6.3** (a) Raman image of a graphene sample acquired by detecting the 2D band Raman intensity, with 488 nm as the excitation wavelength. (b) Temperature dependence of the G-band frequency (filled squares) of single-layer graphene. The solid line is a linear fit of the data. (c) The G-band and 2D band Raman spectra of single-layer graphene at four different temperatures between 295 K and 5 K.

When the temperature decreases from 295 to 5 K, the G band Raman peak of graphene in Figure 6.3 upshifts from 1578.5 to 1585  $\text{cm}^{-1}$ . At same time the 2D band frequency increases from 2693.5 to 2706.5  $\text{cm}^{-1}$ . The temperature dependence of the graphene G band Raman frequency is plotted in Figure 6.3b. The data points are fitted with the following equation,

$$\omega = \omega_0 + c_1 \times T, \quad (6.1)$$

where  $\omega_0$  is the G band frequency at 0 K, and  $c_1$  is the temperature coefficient of graphene. In our data, a temperature coefficient value of  $-0.0186 \text{ cm}^{-1}/\text{K}$  is obtained for the graphene G band. The absolute value of the obtained temperature coefficient is slightly larger than the value of  $-0.016 \text{ cm}^{-1}/\text{K}$ , reported by Calizo et al.<sup>110</sup> for graphene under a temperature range of 83–373 K.

We think this slight difference in the temperature coefficient is mainly caused by the limited number of data points investigated in the present temperature range. Two other possible contributions, the sample temperature difference and charge doping, cannot account for the difference in the temperature coefficient between this work and the work by Calizo et al.<sup>110</sup> First, the relatively lower sample temperature used in the present study should result in a smaller temperature coefficient, since the anharmonic effect in general is weaker at lower temperatures. Second, our graphene sample is probably unintentionally doped. The G mode of doped graphene has been shown to be affected by Kohn anomaly (KA), which softens the phonon frequency.<sup>133</sup> The KA effect is predicted to be stronger at lower (electronic) temperatures,<sup>133</sup> which will result in a phonon downshift in doped graphene at lower  $T$ . This trend is opposite to the phonon upshift arising from anharmonicity when  $T$  decreases and can result in a temperature coefficient of smaller magnitude for lower temperatures. This is in contrast to the observed larger magnitude in this work, suggesting that our graphene sample is only weakly doped, for which the temperature dependence of KA effect has been predicted to be insignificant.<sup>133</sup>

### 6.2.2. Semiconducting tubes

Figure 6.4a shows the room temperature (295 K) and low temperature (5 K) G-band Raman spectra of tube S1, corresponding to the Raman images shown in

Figure 6.2. Tube S1 exhibits an RBM peak at 299 cm<sup>-1</sup> at 295 K, from which the tube diameter can be estimated to be 0.77 nm using the established relationship between RBM frequency  $\omega_{\text{RBM}}$  and tube diameter  $d_t$ ,

$$\omega_{\text{RBM}} = 217.8/d_t + 15.7. \quad (6.2)$$

A (8, 3) chiral index can be assigned to this tube on the basis of its relatively high  $\omega_{\text{RBM}}$ .<sup>75,136</sup> The narrow Lorentzian line shape of the G band is consistent with the semiconducting type of this tube. The G-band Raman spectra were fit with four Lorentzian peaks. When temperature  $T$  is changed from 295 to 5 K, the higher-frequency G<sup>+</sup> Raman peak of this tube at 1583 cm<sup>-1</sup> is found to upshift by  $\sim 2$  cm<sup>-1</sup>, with a concomitant decrease in the line width (full width at half-maximum, FWHM) from 6.5 to 4.5 cm<sup>-1</sup>. Other G-band peaks of this tube show upshift of similar magnitude. The  $\omega_{\text{RBM}}$  of this tube, however, shows a negligible upshift when  $T$  is changed from 295 to 5 K, although its FWHM is narrowed to 3.6 cm<sup>-1</sup> at 5 K from 4.4 cm<sup>-1</sup> at 295 K.

Figure 6.4b compares the 295 and 5 K G-band Raman spectra of another semiconducting nanotube, S2, acquired with 633 nm excitation. At 295 K this tube

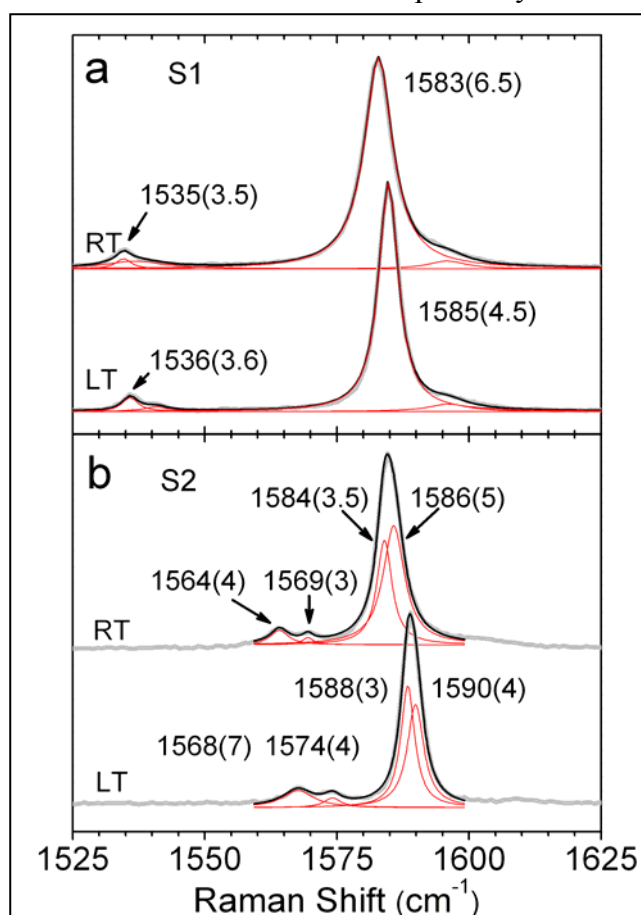


**Figure 6.4** Comparison of room-temperature (RT, 295 K) and low-temperature (LT, 5 K) G-band Raman spectra of two semiconducting nanotubes, S1 (a) and S2 (b). The spectra were fitted with a superposition of four Lorentzian peaks (red curves), with fitted peak positions and line widths (FWHM, in parentheses) in cm<sup>-1</sup> shown in the figure.

shows a weak RBM at  $140 \text{ cm}^{-1}$ , but its intensity is too weak to be resolved at 5 K, due to a change in the resonance Raman condition caused by decreasing temperature.<sup>116,118</sup> The diameter of tube S2 is calculated to be 1.74 nm using equation (6.2), and it is tentatively assigned to (15, 11) or (16, 9) structure. All the G-band Raman peaks of S2 show a relatively large upshift of  $\sim 4 \text{ cm}^{-1}$  when  $T$  is lowered from 295 to 5 K.

The RBM and  $G^+$  peak Raman frequencies at 295 K, and their upshift when  $T$  is changed from 295 to 5 K, for semiconducting tubes S1-7 are listed in Table II, along with their diameter and tentative  $(n, m)$  assignments. Only tubes S1-2 and S6-7 show RBM at 295 K. The diameters of these tubes are determined by using equation (6.2). No RBM mode is observed for tubes S3-5 under 633nm excitation. For these tubes, the frequency difference between the higher-frequency  $G^+$  peak and lower-frequency  $G^-$  peak is instead used to estimate the tube diameter, according to<sup>61</sup>

$$G^+ - G^- = 47.7 \text{ cm}^{-1} \text{ nm}^2 / d_t^2 \quad (6.3)$$

Using this equation and the measured  $G^+ - G^-$  peak separation of  $\sim 21 \text{ cm}^{-1}$ , the diameter of tube S2 is estimated to be  $\sim 1.5 \text{ nm}$ , close to the value determined from its RBM frequency.

### 6.2.3. Metallic nanotubes

We also observed five metallic tubes (M1-5) with 633 nm excitation. The temperature dependent RBM and G band Raman spectra for two metallic tubes, M1 and M3, are shown in Figure 6.5. Tube M1 has an RBM at  $169 \text{ cm}^{-1}$  ( $7.7 \text{ cm}^{-1}$  in FWHM) at 295 K and is tentatively assigned to (18, 0) structure. At 5 K its RBM frequency increases to  $172 \text{ cm}^{-1}$  with a narrowed FWHM of  $6.2 \text{ cm}^{-1}$ . Tube M3 in Figure 6.5c shows an intense RBM at  $213 \text{ cm}^{-1}$  at both 295 and 5 K, suggesting that

the excitation laser energy is in strong resonance with the optical transition energy  $E_{11}^M$  of the tube.<sup>115</sup> M3 can be assigned to (11, 5) structure. Although the RBM frequency of M3 shows little change, its FWHM decreases from  $4.5 \text{ cm}^{-1}$  at 295 K to  $2.8 \text{ cm}^{-1}$  at 5 K. The RBM peak of tube M3 is much narrower than that of tube M1, mainly due to the strong resonance condition and a smaller diameter in M3.<sup>108,115</sup>

The G band Raman

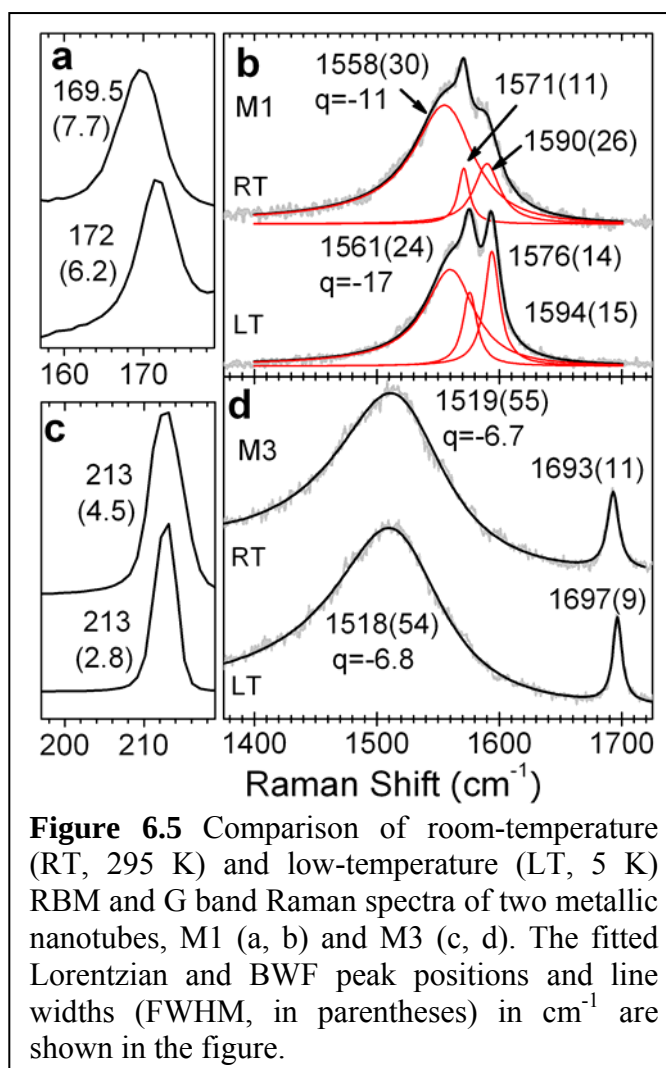


**Figure 6.5** Comparison of room-temperature (RT, 295 K) and low-temperature (LT, 5 K) RBM and G band Raman spectra of two metallic nanotubes, M1 (a, b) and M3 (c, d). The fitted Lorentzian and BWF peak positions and line widths (FWHM, in parentheses) in  $\text{cm}^{-1}$  are shown in the figure.

spectra for tube M1 in Figure 6.5b are fitted by two Lorentzians and a BWF line shape. It can be seen that the G band Raman peaks for M1 upshift by  $3\text{--}5 \text{ cm}^{-1}$  when  $T$  is lowered to 5 K. In addition, the BWF peak becomes narrower and more symmetric ( $|q|$  increases), and its intensity decreases. This observed temperature effect on the G band Raman spectrum for M1 is similar to the previous observation on bundled nanotubes.<sup>137</sup> On the other hand, the G band Raman spectra of the smaller-diameter metallic tube M3 in Figure 6.5d, which can be satisfactorily fitted by a single BWF peak, shows very little change when  $T$  is changed. The BWF Raman feature at 5 K is almost identical to the spectrum at 295 K. However, the peak at  $1693 \text{ cm}^{-1}$ , denoted as  $M$  band in the literature,<sup>138</sup> shows an expected upshift of  $\sim 4 \text{ cm}^{-1}$  at low temperature.

Additional effect other than anharmonicity, e.g., the KA effect as in the case of doped graphene, must also play a role in the temperature dependence of the BWF Raman peak of metallic tubes. This has been shown in the calculation by Piscanec et al.<sup>101</sup>

In metallic tubes, the  $G^+$  component can be assigned to the transverse optical (TO) mode, and the  $G^-$  component (BWF peak) corresponds to the longitudinal optical (LO) mode. KA originates from the coupling of LO phonon with electrons close to the Fermi point. A change in electron temperature will modify the population of these electrons through the Fermi-Dirac distribution, and can renormalize the LO phonon frequency.<sup>101</sup> The metallic tube LO frequency and line width have also been shown to change significantly with the Fermi level of the tube both in literature<sup>92,93,101</sup> and our early data in chapter 5. The difference in the  $T$  dependence of the BWF  $G^-$  (LO) peak between M1 and M3 can be interpreted in terms of different degrees of charge doping, which will be discussed in the following section.

The RBM and  $G^+$  mode frequencies of metallic tubes M1-5, and their shifts when  $T$  is changed from 295 to 5 K, are summarized in Table II. Except for tube M3, the G band Raman spectra of other metallic tubes are fitted by a combination of Lorentzian and BWF lines.

### 6.3. Structural dependence of temperature-induced spectral shift

The temperature dependence of Raman frequencies of a material is due to the anharmonic terms in bond potential energy and involves a volume effect  $(d\omega/dV)_T$  and a pure temperature effect  $(d\omega/dT)_V$ . It is believed that the pure temperature effect is the main contribution to the observed temperature dependence of Raman spectra of SWNTs.<sup>106</sup> The volume effect, on the other hand, is not significant because of the very small thermal expansion coefficient of carbon nanotubes on the basis of

molecular dynamics simulation.<sup>106</sup> In the present study, the effect of SiO<sub>2</sub>/Si substrate thermal stress on the observed SWNT Raman spectral change<sup>139</sup> can be ignored, since the thermal expansion coefficient of SiO<sub>2</sub> film on Si substrate,<sup>140</sup>  $\sim 0.6 \times 10^{-6} / \text{K}$ , is of the same or smaller magnitude compared to those of typical SWNTs.<sup>106</sup> We suggest that the temperature effect observed in this work on the RBM and G band Raman spectra of SWNTs, as in previous studies,<sup>106,108</sup> arises from the temperature dependence of the bond force constants in SWNTs.

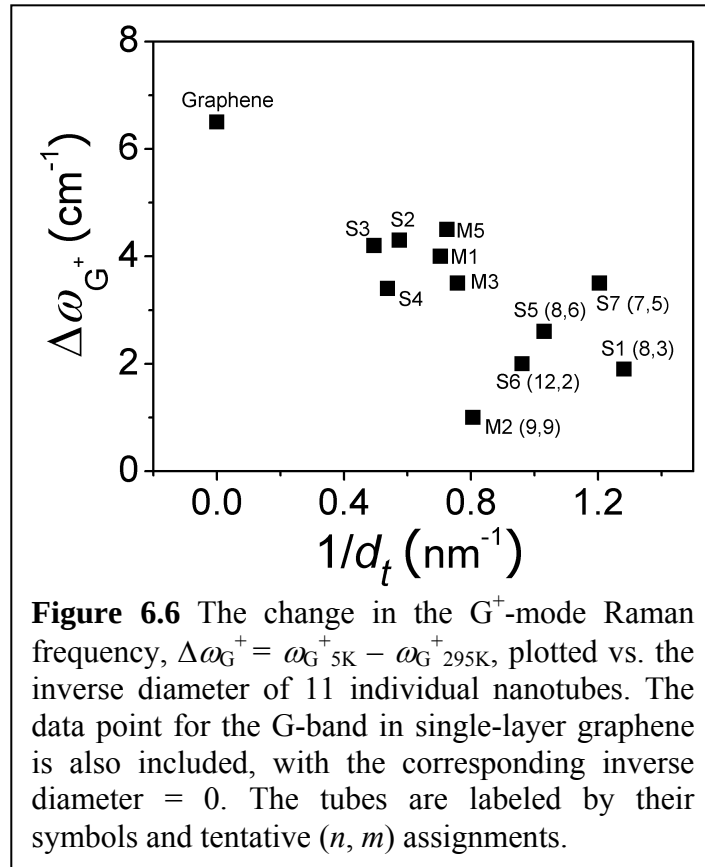
The results obtained in the present study are consistent with the previous temperature-dependent Raman scattering studies on bundled and isolated SWNTs,<sup>105-108,113,114,137</sup> which revealed that both RBM and G-band Raman spectra of SWNTs exhibit a downshift with increasing temperature, as observed in bulk semiconductor materials.<sup>123,141,142</sup> Our results on individual tubes allow us to study how the structure of a nanotube influences its temperature-induced Raman frequency shift. For example, the results obtained in this work suggest that the temperature-induced RBM and G band Raman spectral change of individual nanotubes depends on the tube diameter. As seen above, smaller-diameter tubes tend to show negligible change when  $T$  is lowered to 5 K, while larger-diameter tubes exhibit a more significant temperature effect.

### 6.3.1. Temperature-induced G band Raman spectral shift

Since the G band Raman spectra of semiconducting tubes are not influenced by electron-phonon coupling, the temperature-induced G mode Raman frequency upshift is only due to the anharmonic effect and not affected by KA.<sup>101,102</sup> Although the metallic tube G<sup>+</sup> (TO) mode is affected by KA, it has been shown from dynamical calculation that, unlike G<sup>-</sup> (LO), the KA effect in G<sup>+</sup> (TO) is temperature

independent.<sup>101,102</sup> The G mode in doped graphene is also affected by KA.<sup>133</sup> However, for undoped or slightly doped graphene, it has been shown that the temperature dependence of KA is negligible, although this effect is more significant for doped graphene with Fermi energy close to  $1/2\hbar\omega_G$ .<sup>133</sup> Our graphene sample is at most only slightly doped as judged from the G mode frequency, line width, and the temperature coefficient. The observed temperature induced change in the graphene G mode and metallic tube  $G^+$  (TO) mode can thus be attributed to anharmonic effect, and can be compared with the change in the semiconducting tube  $G^+$  (LO) peak.

To look at the tube diameter dependence of the upshift in  $G^+$  mode frequency, in Figure 6.6 we display  $\Delta\omega_G^+ = \omega_G^+_{5K} - \omega_G^+_{295K}$  for semiconducting tubes S1-7 and the metallic tubes that show  $G^+$  peak, plotted against their inverse diameter. The data point for graphene is also included with the corresponding inverse diameter = 0. A clear trend of diameter dependence for  $\Delta\omega_G^+$  is revealed from Figure 6.6. In general, larger-diameter tubes such as S2 and S3 tend to exhibit higher  $\Delta\omega_G^+$ . SLG can be thought of as a tube with infinity diameter, and it indeed shows the highest G band Raman frequency change. The  $G^+$  band Raman peaks of the semiconducting tubes S1-7 show an upshift  $\Delta\omega_G^+$  between 1 and 5  $\text{cm}^{-1}$  when  $T$  is lowered from 295



to 5 K. The average upshift is around  $3.1 \text{ cm}^{-1}$ , which gives an estimated average temperature coefficient  $d\omega/dT \sim -0.011 \text{ cm}^{-1}/\text{K}$  for the  $G^+$  peak of semiconducting tubes. The absolute value of the obtained temperature coefficient is smaller than the previous value of bulk samples of SWNTs measured at higher temperatures from 300 to 800 K.<sup>106</sup> This is expected because the anharmonic effect is more significant at higher temperatures.

The observed diameter dependence of the temperature induced Raman frequency change  $\Delta\omega_G^+$  reflects that the temperature dependence of C-C bond force constants is weaker for smaller-diameter nanotubes, suggesting that the C-C bonds in smaller-diameter nanotubes is more difficult to be hardened upon temperature decrease.<sup>108</sup> This can be understood from the fact that the nanotube curvature induces  $sp^3$  character to the C-C bonds in SWNTs, with smaller-diameter tubes having more  $sp^3$  components. Thus the behavior of smaller-diameter tubes should deviate more from graphene, as observed in Figure 6.6, in the case of the G-band frequency shift  $\Delta\omega_G^+$  arising from the temperature change.

In Figure 6.6, the data points for small-diameter tubes such as S1 and S5-7 are much scattered, suggesting that the temperature-induced G band Raman frequency change  $\Delta\omega_G^+$  also depends on the chirality of the tube. The chirality effect on  $\Delta\omega_G^+$  is more significant especially for small-diameter tubes. Figure 6.6 seems to suggest that MOD2 tubes may have higher  $\Delta\omega_G^+$  when  $T$  is lowered. Of those small-diameter tubes studied, tube S7, which is assigned to (7, 5) structure, seems noteworthy. The tube displays a relatively larger G band frequency upshift  $\Delta\omega_G^+$  when  $T$  is changed from 295 to 5 K, yet its RBM exhibits a negligible shift for the same temperature change. A definite relation between the tube chirality and the temperature-induced G

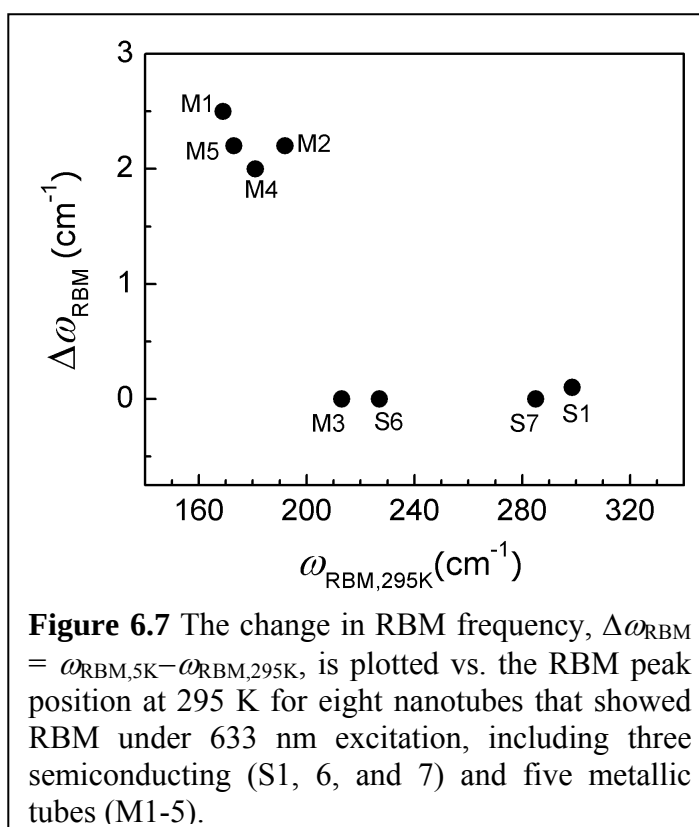
band Raman frequency change is difficult to establish at present due to the insufficient number of chiral structures in this work.

### 6.3.2. Temperature-induced RBM shift

Temperature induced RBM frequency change also exhibits a tube-diameter dependence. The upshift in RBM frequency when  $T$  is changed from 295 to 5 K,  $\Delta\omega_{\text{RBM}} = \omega_{\text{RBM},5\text{K}} - \omega_{\text{RBM},295\text{K}}$ , is shown in Figure 6.7 for eight tubes (M1-5, S1, 6, 7) that display RBM under 633 nm excitation. It can be seen that  $\Delta\omega_{\text{RBM}}$  for small-diameter tubes with  $\omega_{\text{RBM},295\text{K}} > 210 \text{ cm}^{-1}$  (e.g., S1, 6, 7 and M3) is negligible, while

large-diameter tubes with  $\omega_{\text{RBM},295\text{K}} < 200 \text{ cm}^{-1}$  (e.g., M1, 2, 4, 5) exhibit  $\Delta\omega_{\text{RBM}} \sim 2.5 \text{ cm}^{-1}$  when  $T$  is lowered from 295 to 5 K. The diameter dependence of temperature-induced RBM frequency change has been observed previously on double-wall carbon nanotubes (DWNTs)<sup>143,144</sup>

and suspended individual SWNTs.<sup>108</sup>



As discussed above, the volume effect on temperature-induced RBM shift can be neglected because the thermal expansion of SWNTs is very small over the experimental temperature range in this work. In the bond force constant model, the RBM frequency  $\omega_{\text{RBM}}$  is related to the C-C bond force constant  $\Phi$  by<sup>143,145</sup>

$$\omega_{\text{RBM}} = \frac{2a_{\text{C-C}}\sqrt{\Phi}}{\sqrt{md}}, \quad (6.4)$$

where  $a_{\text{C-C}}$  is the C-C bond length,  $m$  is the mass of carbon atom, and  $d$  is the diameter of the tube. Apparently the temperature dependence of the force constant  $\Phi$  will lead to a change in the RBM (and the G band) Raman frequencies of SWNTs. However, a numerical analysis using the bond force model shows that the temperature dependence of the C-C bond force constants alone cannot explain the observed magnitude of RBM frequency shift, in particular for larger-diameter SWNTs. Since the observed G band frequency upshift of SWNTs in the present study is similar to the results obtained by Raravikar et al.,<sup>106</sup> we adopt the same temperature dependent C-C bond-stretching force constant and bond-bending force constant, as derived by Raravikar et al., to calculate the temperature dependence of G-band and RBM frequency of a nanotube. It is found that  $\Delta\omega_{\text{RBM}}$  arising from the temperature dependence of the bond force constant is much smaller than  $\Delta\omega_{\text{G}}^+$  over the same temperature range. For a tube with a diameter of 1.34 nm, the shift in RBM frequency is only about  $0.6 \text{ cm}^{-1}$  while the corresponding change in G mode is  $5.5 \text{ cm}^{-1}$  when  $T$  is changed from 295 to 5 K. The observed relatively larger  $\Delta\omega_{\text{RBM}}$  for tubes of similar diameter in the present study cannot be attributed only to the temperature dependence of C-C bond force constants. Other factors must be considered in order to account for  $\Delta\omega_{\text{RBM}}$  observed for larger-diameter tubes in this work.

#### 6.4. Tube-substrate interaction

The observation of temperature-induced RBM frequency upshift (Figure 6.7) suggests the existence of a diameter threshold. In general, tube-substrate interaction can result in the radial deformation of the adsorbed nanotubes.<sup>58,146</sup> Prior molecular

mechanics simulation revealed that the tube-substrate binding energy and the extent of the cross-sectional deformation increases dramatically with increasing tube diameter.<sup>146</sup> The tube-substrate interaction has been invoked to explain the Raman spectra variations observed on partially supported nanotubes<sup>147,148</sup> and has been further used to introduce strain into nanotubes.<sup>149</sup> We suggest that this diameter dependent tube-substrate interaction contributes to the temperature-induced RBM frequency shift of individual nanotubes observed in this work, especially for larger-diameter tubes. Tube-substrate interaction is expected to have a more dramatic effect on RBM frequency than on the G-band frequency of a nanotube, because the RBM has the vibrational component perpendicular to the substrate. Larger-diameter tubes will experience a stronger interaction with the substrate due to the severe flattening-deformation of the tube. We think that the contribution from the tube-substrate interaction to the observed RBM shift in larger-diameter tubes dominates over the contribution from the temperature dependence of C-C bond force constants based on the estimation just discussed above.

### 6.5. Temperature dependence of BWF peak in metallic tubes

There are two contributions to the metallic  $G^-$  (LO) mode (BWF peak) change induced by temperature variation, the anharmonic effect and the effect arising from KA.<sup>101</sup> The anharmonic effect can be taken to be the same as the  $G^+$  peak in metallic or semiconducting tubes. SWNTs used in the present study are likely unintentionally charge doped to different degrees, as implied by the variation in  $G^-$  (LO) peak frequency and line width for individual metallic tubes (chapter 4). For example, here M1 tube has  $G^-$  peak at  $1558\text{ cm}^{-1}$  with a width of  $\sim 30\text{ cm}^{-1}$ , while M3 shows a  $G^-$  peak at  $1519\text{ cm}^{-1}$  with a width  $\sim 55\text{ cm}^{-1}$ . The much broader  $G^-$  peak in M3 tube

indicates a less charge doping in this tube. Moreover, the change of  $G^-$  (LO) mode position and line width of metallic tubes with its Fermi level has been calculated for different temperatures using time-dependent perturbation theory,<sup>101,102</sup> which is also shown in Figure 5.1. On the basis of this calculation, the observed difference in the temperature dependence of  $G^-$  (LO) peak between M1 and M3 can be rationalized as arising from the different degrees of charge doping. The  $G^-$  peak position of M1 blueshifts by  $\sim 3 \text{ cm}^{-1}$  when  $T$  is changed from 295 to 5 K. If the anharmonic contribution is  $\sim 3\text{-}4 \text{ cm}^{-1}$ , then the shift due to temperature-dependent KA is about zero. From the calculation, the Fermi level  $|\epsilon_F|$  in tube M1 can be estimated to be slightly above  $1/2\hbar\omega_G$ . On the other hand, M3 tube shows a very broad and stable  $G^-$  peak. If taking the anharmonic contribution of the peak shift to be  $\sim 4 \text{ cm}^{-1}$ , the observation of a stable  $G^-$  peak in M3 when  $T$  is lowered from 295 to 5 K indicates that the shift due to KA should be around  $-4 \text{ cm}^{-1}$ . This suggests that M3 tube is doped to a less degree compared with M1, with an estimated Fermi level  $|\epsilon_F|$  slightly below  $1/2\hbar\omega_G$ . To test this scenario, further study of the evolution of the G band Raman peak with the Fermi level of individual metallic tubes, carried out at different low temperatures, is underway.

## 6.6. Summary

In summary, we have obtained Raman spectra for 12 individual carbon nanotubes of differing diameter on Si/SiO<sub>2</sub> substrates at both 295 and 5 K, and the Raman spectra of single layer graphene over a temperature range from 295 to 5 K. In general both RBM and the  $G^-$  band Raman peaks exhibit an upshift on decreasing temperature. The average upshift in the  $G^-$  band frequency of semiconducting nanotubes is  $3.1 \text{ cm}^{-1}$  when temperature is changed from 295 to 5 K, with a

corresponding estimated temperature coefficient  $d\omega/dT \sim -0.011 \text{ cm}^{-1}/\text{K}$ . It is found that the temperature induced G band Raman frequency change of SWNTs depends on the tube diameter, with larger-diameter tubes typically exhibiting a higher Raman frequency upshift on decreasing temperature. The temperature-induced shift in the G band frequency of single layer graphene is found to be greater than those in carbon nanotubes. The observed diameter dependence in the case of temperature induced G band frequency shift is explained as arising from the temperature dependence of C-C bond force constants in SWNTs, which is influenced by the nanotube curvature. However, the diameter dependent tube-substrate interaction is proposed to be the main factor in contributing to the diameter dependence of the temperature-induced RBM frequency change observed in this work. Evidence of chirality dependence of the temperature dependent Raman scattering in SWNTs is also revealed in this work. The observed difference in the temperature dependence of the  $G^-$  BWF peak position and line width of different individual metallic tubes can be rationalized in the context of charge doping and Kohn anomaly. We note that the conclusions derived from this work are based on a small number of individual tubes investigated and is preliminary only. Further measurements, for example, by using tunable laser wavelengths to access more tubes with different  $(n, m)$  structure, and at various low temperatures, are necessary to generalize the results obtained in the present work.

## Chapter 7

### Second-order Raman scattering: combination modes

The previous chapters have focused on the prominent first-order Raman features of SWNTs, which include the radial breaching mode (RBM) at  $\sim 200\text{ cm}^{-1}$  and tangential C–C stretching mode (G band) at  $\sim 1590\text{ cm}^{-1}$ . In addition to these well-characterized RBM and G band first-order Raman features, SWNTs also exhibit many second-order and higher-order Raman modes.<sup>138,150-152</sup> Some important second-order features, which include the disorder-induced D band at  $\sim 1350\text{ cm}^{-1}$  and the so-called G' mode at  $\sim 2700\text{ cm}^{-1}$ , the overtone of D mode, have received considerable attention.<sup>153</sup> The G' mode has recently been shown to provide information on charged defects in SWNTs.<sup>154</sup> In graphene, a material closely relevant to SWNTs, the line shape of the G' mode can be used to determine the number of graphene layers.<sup>127,130</sup> However, the multiple second-order Raman features between  $1650$  and  $2000\text{ cm}^{-1}$  in the Raman spectra of SWNTs such as the M band and the iTOLA mode have received only limited attention,<sup>138,155,156</sup> mostly because of their low Raman intensity.

The feature around  $1750\text{ cm}^{-1}$ , often consisting of a double-peak shape in ensemble measurement and thus designated as the M band,<sup>138</sup> has been interpreted as the overtone of the graphite out-of-plane transverse optical (oTO) mode at  $867\text{ cm}^{-1}$ . The features at  $\sim 1950\text{ cm}^{-1}$  have been attributed to the combination of the graphite in-plane transverse optical phonon (iTOL) and longitudinal optical phonon (LO), with the longitudinal acoustic (LA) phonon, thus called iTOLA and LOLA modes, respectively.<sup>138,155</sup> They will be simply called iTOLA hereafter. In addition, the combination mode involving the G band and RBM of SWNTs (G+RBM) is also

expected to appear between 1650 and 2000  $\text{cm}^{-1}$  and has been identified in the Raman spectra of individual small bundles of SWNTs.<sup>156</sup>

In ensemble Raman measurement, the M band frequency is slightly sensitive to excitation wavelength.<sup>138,157</sup> At the single nanotube level, the M band has recently been found independent of the excitation wavelength.<sup>158</sup> Similar to the D mode and G' mode, however, the iTOLA band of a bulk SWNT sample is highly dispersive with laser excitation wavelengths,<sup>138,157</sup> and a double-resonance Raman mechanism has usually been proposed to explain this dispersive behavior.<sup>35,159,160</sup> An unsolved issue essential to the double-resonance mechanism is whether the dispersive nature of the iTOLA mode observed in ensemble measurement is intrinsic to SWNTs and will persist at the single nanotube level.

In the present work, we examine second-order Raman features, mainly the M band and iTOLA band, between 1650 and 2000  $\text{cm}^{-1}$  of individual nanotubes on Si/SiO<sub>2</sub> substrates. We focus on relatively small-diameter nanotubes with RBM frequencies higher than 190  $\text{cm}^{-1}$ . The chirality ( $n$ ,  $m$ ) of these small-diameter tubes can be assigned reliably on the basis of their RBM frequencies and intensities, thus allowing us to unravel the structural dependence of second-order Raman modes in these SWNTs. We measure the Raman spectra of individual tubes using multiple excitation wavelengths. In contrast to ensemble Raman measurements on SWNTs, the M band and iTOLA band of individual tubes are discovered to be non-dispersive (i.e., Raman frequencies are independent of the excitation wavelength). Because of the resonance enhancement effect associated with the exciton transition of a nanotube, unusual Raman spectra with enhanced second-order modes (M band or iTOLA band) are observed in some single tubes. It is also observed that the relative intensity of the M band and iTOLA mode depends on the chirality and family type of a nanotube.

Moreover, the G+RBM combination mode is clearly identified in small-diameter semiconducting tubes. Low-temperature Raman spectroscopy is further used to resolve the fine structure of the M band and iTOLA modes. These second-order Raman modes thus provide information on the chirality and electronic structure of SWNTs and can help in determining the structure of SWNTs from Raman spectroscopy.

### 7.1. General observation of M band, G+RBM mode and iTOLA mode

Raman spectra of more than 100 tubes or small bundles synthesized by CVD on several Si/SiO<sub>2</sub> substrates were first measured with 633 nm excitation. The spectra of about 54 presumably single tubes showed only one peak in the RBM region. Their G band Raman spectra were also indicative of single tubes being probed. G band Raman spectra of several such tubes are shown in Figure 7.1. Corresponding RBM frequencies are also indicated in Figure 7.1 for these tubes. From bottom to top, the spectra represent a large-diameter semiconducting tube, two intermediate-diameter metallic tubes, and five small-diameter semiconducting tubes, respectively. Multiple second-order Raman features with various intensities can be observed between 1650 and 2000 cm<sup>-1</sup> in these spectra.

Figure 7.2 summarizes the observed second-order Raman frequencies between 1650 and 2000 cm<sup>-1</sup> of these 54 individual tubes as a function of inverse diameter. As indicated in the Figure 7.2, the second-order Raman frequencies of these studied individual SWNTs fall into three groups. The modes between 1650 and 1790 cm<sup>-1</sup> can be assigned to the M band, and those from 1890 cm<sup>-1</sup> to 2000 cm<sup>-1</sup> are the iTOLA band of different nanotubes. The third group consists of Raman mode with frequencies between 1790 and 1890 cm<sup>-1</sup>, observed clearly only for small-diameter

semiconducting tubes. As discussed below, this third group can be assigned to the combination of G band with the RBM of an individual tube.

Figure 7.2 reveals that most large-diameter tubes with  $d_t > 1.0 \text{ nm}^{-1}$  exhibit only the M band, and their iTOLA band is generally too weak and not detected. This agrees with the previous observation of individual nanotubes with  $0.45 \text{ nm}^{-1} < d_t < 0.75 \text{ nm}^{-1}$  reported by Brar et al.<sup>138</sup> However, the majority of small-diameter tubes with  $d_t \leq 1.0 \text{ nm}^{-1}$ , mostly semiconducting nanotubes,

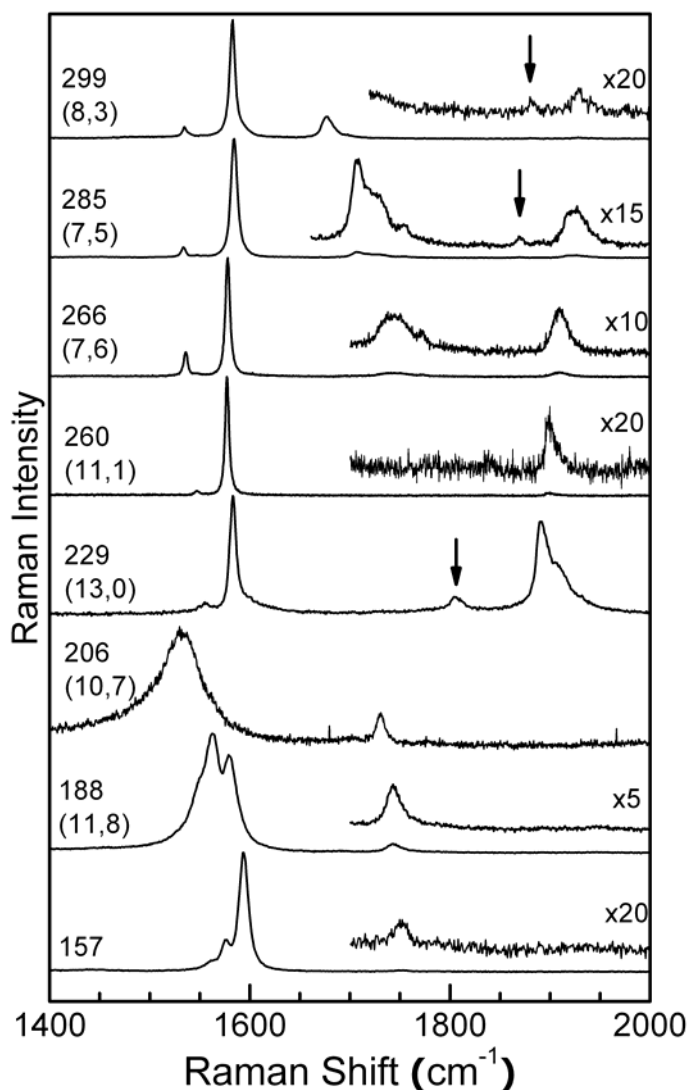
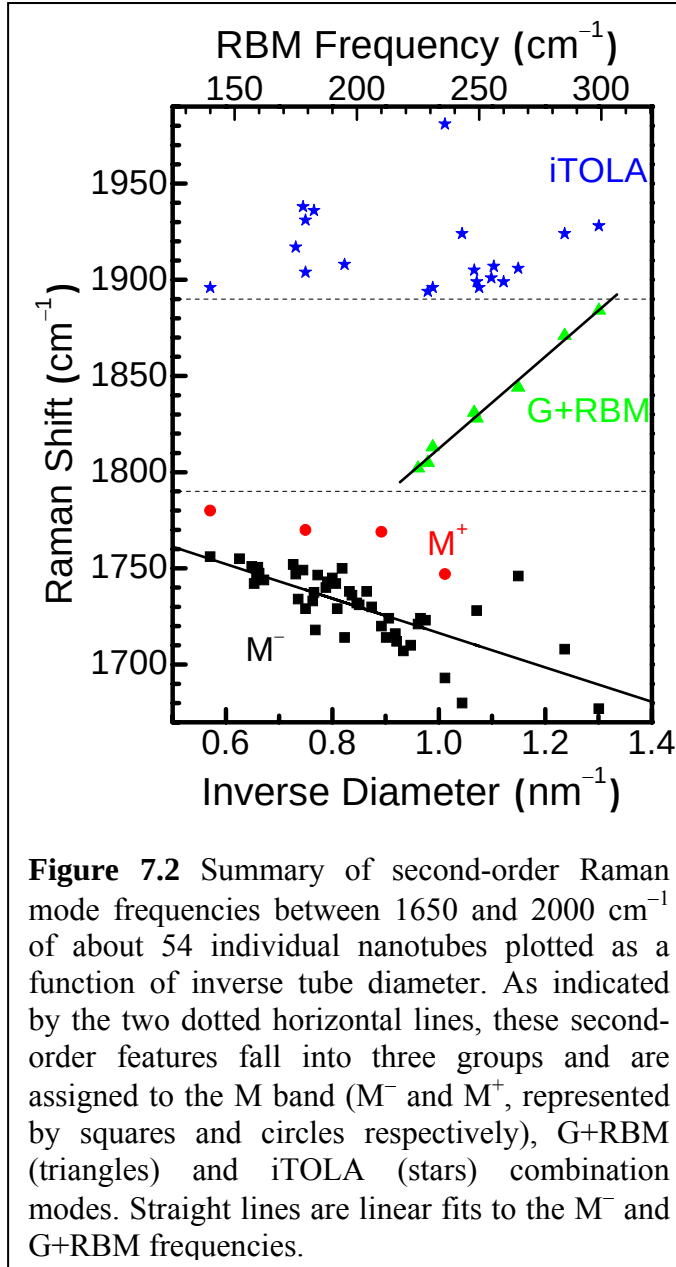


**Figure 7.1** Raman spectra between 1400 and 2000  $\text{cm}^{-1}$  of eight individual single-wall carbon nanotubes obtained with 633 nm laser excitation, showing the G band and second-order Raman features. The corresponding RBM frequency and tentative  $(n, m)$  assignment for each tube are labeled above each spectrum. Arrows indicate the G+RBM combination mode observed in some small-diameter tubes. The spectra are normalized to the strongest G band peak of each tube.

exhibit the iTOLA band and G+RBM mode as well as the M band. The M band frequencies of these small-diameter tubes, ranging from  $\sim 1670$  to  $\sim 1770 \text{ cm}^{-1}$ , are more scattered compared with those of large-diameter tubes. It is also found that the M band of single tubes in general consists of only one peak. The M band consisting of

two peaks, often seen in ensemble measurements,<sup>138</sup> is observed only in four tubes out of the 54 single tubes analyzed here. We adopt the convention to designate the single-peak M band and the lower-frequency feature of the double-peak M band as  $M^-$  and the higher frequency feature of the double-peak M band as  $M^+$ .<sup>138</sup>  $M^+$  and  $M^-$  are included in Figure 7.2, which also shows that the M band frequencies of single tubes slightly increase with tube diameter. A linear fit of the  $M^-$  mode frequencies in Figure 7.2 yields the equation

$$\omega_{M^-}(\text{cm}^{-1}) = -89.6/d_t(\text{nm}) + 1806.$$



As highlighted by arrows in Figure 7.1, a Raman feature located between 1790 and 1890  $\text{cm}^{-1}$  is clearly resolved in several small-diameter semiconducting tubes (as an example, see the spectrum assigned to (13, 0) in Figure 7.1). The frequency of this Raman mode shows a linear dependence on the inverse tube diameter, which is also shown in Figure 7.2, and can be fitted satisfactorily by

$$\omega_{G+RBM}(\text{cm}^{-1}) = 239.4/d_t(\text{nm}) + 1573.$$

Note that the constant  $1573 \text{ cm}^{-1}$  is very close to the  $G^+$  mode frequency of small-diameter tubes and the term  $239.4/d_t$  agrees well with the previously established empirical relation between the RBM frequency and diameter of SWNTs,<sup>32</sup>  $\omega_{\text{RBM}} = 248/d_t$ . Thus, the Raman features between  $\sim 1790$  and  $\sim 1890 \text{ cm}^{-1}$  observed in small-diameter tubes are assigned to the combination of G band with RBM (G+RBM). It is further found that the frequency of this mode is in excellent agreement with the sum of the RBM and  $G^+$  frequencies for each of these small-diameter tubes, thus confirming the assignment to G+RBM. The G+RBM combination mode was initially proposed as a possible assignment for the observed M band Raman feature<sup>151</sup> because of the similar frequencies of these two modes for large-diameter tubes. The present work shows that the G+RBM mode of a single nanotube in general is much weaker than the M band and iTOLA band. Identification of G+RBM mode in small-diameter tubes is facilitated by the increased separation of this mode from the M band. This G+RBM mode was also observed previously in Raman spectra of individual SWNT bundles reported by Zhao et al.<sup>156</sup>

## 7.2. Excitation wavelength dependence of M band and iTOLA mode

Previous ensemble Raman spectra measurements on SWNTs have observed that the iTOLA mode is highly dispersive, with its frequency increasing with excitation laser energy, while the M band is only slightly dispersive.<sup>138,157</sup> Brar et al. reported that the iTOLA frequency of a bulk SWNT sample increased from  $1864 \text{ cm}^{-1}$  with 1.58 eV excitation to  $1987 \text{ cm}^{-1}$  with 2.41 eV excitation.<sup>138</sup> A similar observation on ensemble SWNTs was reported recently.<sup>157</sup> To determine whether this dispersive behavior of the iTOLA mode and M band is preserved at the single nanotube level, we used multiple laser wavelengths to measure Raman spectra of the same individual

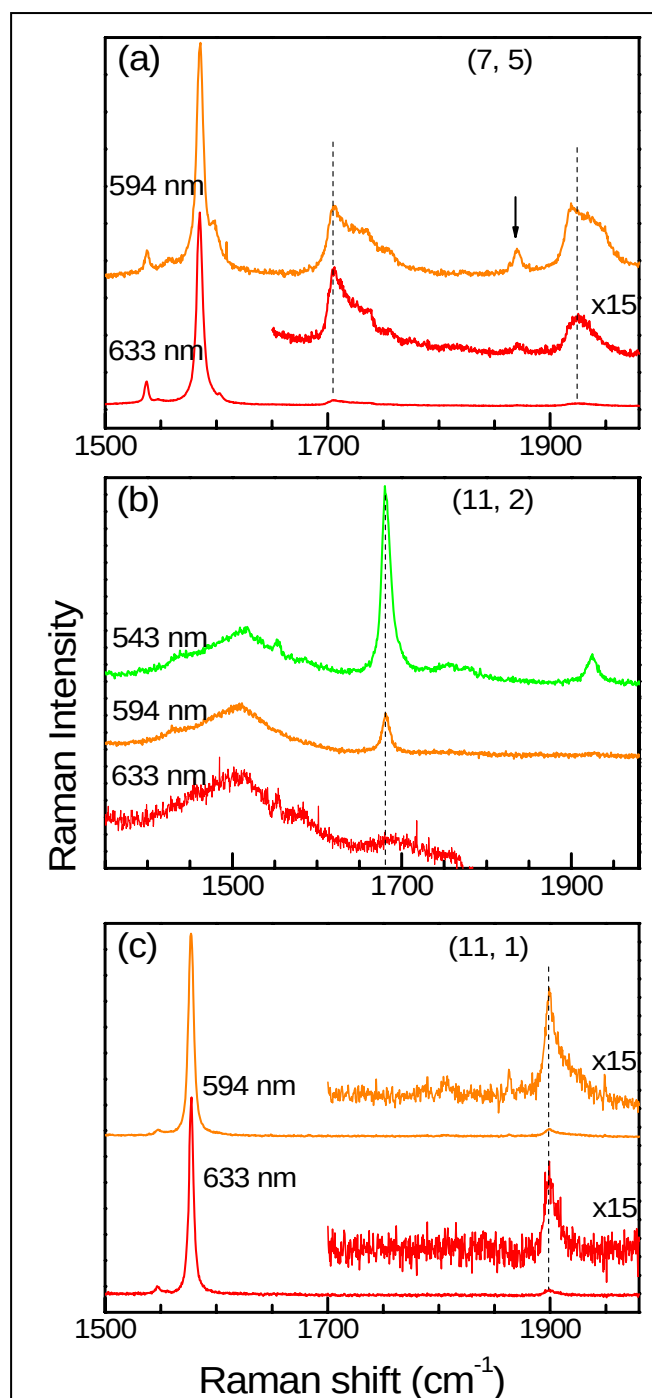


**Figure 7.3** Excitation wavelength dependent Raman spectra of three individual tubes: (a) a semiconducting tube (7, 5); (b) a metallic tube (11, 2); and (c) a semiconducting tube (11, 1). Spectra were acquired using laser wavelengths of 633, 594, and 543 nm. The arrow in (a) indicates the weak G+RBM combination feature. All spectra are normalized to the G-band peak of each tube.

tubes. If an excitation energy dependence the same as the bulk SWNT sample is assumed for a single tube, a shift in the iTOLA frequency of  $\sim 20 \text{ cm}^{-1}$  would be expected for the single tube when the excitation wavelength is changed from 633 to 594 nm.

Figure 7.3 shows Raman spectra of two semiconducting tubes and a metallic tube, measured using different excitation wavelengths. Such excitation wavelength-dependent measurement also facilitates the  $(n, m)$  assignment for these individual tubes. The tubes in Figure 7.3 are assigned to (7, 5), (11, 2), and (11, 1), respectively, on the basis of their RBM frequencies and intensities at various excitation energy  $E_{\text{laser}}$ , according to the Kataura plot reported by Son et al.<sup>54</sup> It can be

seen that the intensities of the M band and iTOLA band relative to the respective G

band are sensitive to  $E_{\text{laser}}$ , and a shoulder develops at the high-energy side of the iTOLA band when the excitation wavelength is decreased. However, within experimental uncertainty, the peak frequencies of the M band and iTOLA band are independent of the excitation wavelength. This excitation energy independence of the M band and iTOLA band is also observed on other individual tubes using 594, 543, and 514 nm as the excitation. This behavior of single nanotubes is in contrast to the highly dispersive nature of the iTOLA band of bulk SWNT samples. It suggests that the previously observed dispersive behavior in ensemble Raman measurement is most likely due to the excitation of different tubes as the laser wavelength is changed. In a relevant resonant Raman excitation study by Walsh et al.,<sup>158</sup> M band frequencies of two single nanotubes were also found to be independent of the excitation wavelength, in agreement with the present work.

Figure 7.3 also shows that Raman relative intensity of the second-order modes to the G band increases when the excitation wavelength is decreased, demonstrating a resonance behavior for the M band and iTOLA band of an individual nanotube. Because of the uncertainty in the absolute Raman intensity caused by sample drifting during spectral measurement and variation in the detection efficiency for different laser wavelengths, and also as the Raman spectra in Figure 7.3 are all normalized to the G band, we compare relative intensities  $I_{\text{M}}/I_{\text{G}}$  and  $I_{\text{iTOLA}}/I_{\text{G}}$  as a function of laser energy to examine the resonance profiles of the M and iTOLA modes of individual tubes. We focus on small-diameter tubes with a RBM frequency higher than  $200 \text{ cm}^{-1}$  because the chirality ( $n, m$ ) can be assigned to these tubes reliably, in a similar manner as used for the tubes in Figure 7.3. Excitation wavelength-dependent Raman measurements were performed on about 10 such tubes, including both metallic and semiconducting tubes.

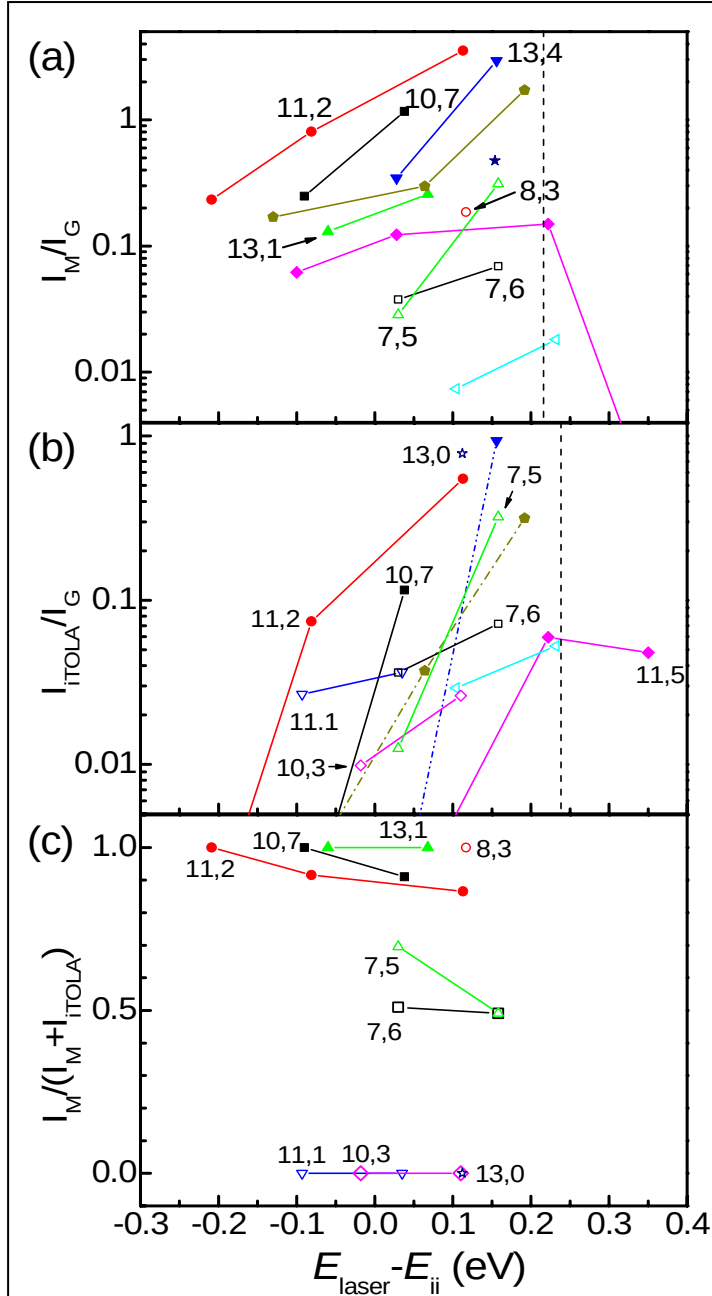


**Figure 7.4** Raman intensity ratio of (a)  $M^-$  band over G band,  $I_M/I_G$ ; (b) iTOLA band over G band,  $I_{\text{iTOLA}}/I_G$ ; and (c)  $I_M/(I_M + I_{\text{iTOLA}})$ , of single metallic (filled symbols) and semiconducting (open symbols) nanotubes, as a function of  $E_{\text{laser}} - E_{\text{ii}}$ . The points for the same tube are connected by lines. The vertical dotted lines in (a) and (b) represent the average phonon energy of the M band and the iTOLA band, respectively, of studied individual tubes.

In Figure 7.4a and b, the intensity ratios  $I_M/I_G$  and  $I_{\text{iTOLA}}/I_G$  of these tubes are plotted as a function of  $E_{\text{laser}} - E_{\text{ii}}$ . Here  $E_{\text{laser}}$  and  $E_{\text{ii}}$  are the laser photon energy and electronic transition energy of a nanotube. For the laser wavelengths used in this work,  $E_{\text{ii}}$  represents  $E_{11}^M$  and  $E_{22}^S$  for small-diameter metallic and semiconducting nanotubes, respectively. The calculated  $E_{11}^M$  and  $E_{22}^S$  values in the Kataura plot by Son et al.<sup>40</sup> are found to agree very well with experimental values determined by resonance Raman spectroscopy for SWNTs synthesized by CVD method on a quartz substrate.<sup>55</sup> In our study,

the experimental values of  $E_{\text{ii}}$ , if available, are used in Figure 7.4. When an experimental value is not available for a nanotube, the calculated  $E_{\text{ii}}$  from the Kataura

plot of Son et al.<sup>40</sup> are then used. Data points for the same tube corresponding to different  $E_{\text{laser}}$  values are connected by lines in Figure 7.4.

For tubes whose Raman spectra are measured with two or more different  $E_{\text{laser}}$  values, it is shown that their intensity ratios  $I_{\text{M}}/I_{\text{G}}$  and  $I_{\text{iTOLA}}/I_{\text{G}}$  increase significantly as  $E_{\text{laser}}$  is moved above  $E_{\text{ii}}$ , indicating a resonance excitation behavior for the M and iTOLA bands different from the G band excitation profile. Because the M band is associated with the overtone of the graphite oTO mode at  $\sim 867 \text{ cm}^{-1}$ , resonances at  $E_{\text{laser}} = E_{\text{ii}}$ ,  $E_{\text{ii}} + E_{\text{oTO}}$ , and  $E_{\text{ii}} + 2E_{\text{oTO}}$  are expected to occur for the M band.<sup>152</sup> Because  $E_{\text{laser}} = E_{\text{ii}}$  is also the resonance condition for the first-order G mode, we expect that the intensity ratio  $I_{\text{M}}/I_{\text{G}}$  will show resonances at  $E_{\text{laser}} = E_{\text{ii}} + E_{\text{oTO}}$  and  $E_{\text{ii}} + 2E_{\text{oTO}}$ , at which the G mode is not in resonance. The distribution of intensity ratios  $I_{\text{M}}/I_{\text{G}}$  of individual tubes shown in Figure 7.4a is more consistent with the scattering photon resonance condition  $E_{\text{laser}} = E_{\text{ii}} + 2E_{\text{oTO}}$  ( $E_{\text{M}}$ ). A similar analysis for the iTOLA band, shown in Figure 7.4b, also suggests a scattering resonance  $E_{\text{laser}} = E_{\text{ii}} + E_{\text{iTOLA}}$  for this mode. Panels a and b of Figure 7.4 also show that the M band and iTOLA band have significantly overlapped resonance excitation profiles, apparently because of the small difference in the frequencies of these two modes.

Due to the different resonance conditions for the second-order M band and iTOLA band from the first-order G mode, it is possible to observe some unusual Raman spectra with enhanced second-order modes such as the spectrum of the (13, 0) tube shown in Figure 7.1 and that of the (11, 2) tube excited with 543 nm shown in Figure 7.3b. This type of unusual Raman spectra had never been observed in ensemble measurements because the ensemble spectra are always dominated by the intense resonant first-order G mode. Recently Wang et al. observed higher-order multi-phonon Raman scattering with intensities comparable to the first-order G band

from suspended individual SWNTs.<sup>152</sup> They also showed that the scattering photon resonance was important to the enhancement of higher-order Raman mode intensities. Walsh et al. reported the use of scattering photon resonance in the M band Raman excitation spectroscopy to determine  $E_{ii}$  of individual nanotubes.<sup>158</sup> The present work is in agreement with both of these studies.

### 7.3. Structure dependence of Raman intensities

It is apparent from panels a and b of Figure 7.4 that the M band and iTOLA mode Raman intensities vary significantly for different tubes, even if they have similar resonance conditions in terms of  $E_{\text{laser}} - E_{ii}$ . This implies that the intensities of the M band and iTOLA band also depend on the chirality of a nanotube. This chirality dependence of the M band and iTOLA mode intensities is more clearly revealed by inspecting the relative Raman intensity of these two modes in small-diameter tubes, especially the semiconducting ones. The Raman intensity ratio  $I_M / (I_M + I_{\text{iTOLA}})$  is calculated for the Raman spectra of small-diameter tubes and is shown in Figure 7.4c for several tubes as a function of  $E_{\text{laser}} - E_{ii}$ . For metallic tubes, iTOLA band is typically very weak in comparison with M band. The latter is often the dominant second-order feature between 1650 and 2000  $\text{cm}^{-1}$  in metallic tube Raman spectra. For semiconducting tubes, the MOD2 near-zigzag tubes such as (13, 0), (11, 1) and (10, 3) often exhibit an iTOLA band much more intense than the M band of the same tubes, with the respective ratio  $I_M / (I_M + I_{\text{iTOLA}}) \approx 0$  in Figure 7.4c. In particular, as shown in Figure 7.1, the second-order iTOLA band of a (13, 0) tube is almost as intense as the first-order G band, while its M band is not detected. In contrast, the MOD1 near-zigzag semiconducting tubes such as the (8, 3) tube whose spectrum is also shown in Figure 7.1 possess an M band more intense than the iTOLA band. Walsh et al.

previously also observed a strong M band at  $1734\text{ cm}^{-1}$  in (12, 4) and (13, 2) tubes (their iTOLA bands were not shown),<sup>158</sup> both of which are MOD1 near-zigzag semiconducting tubes, thus supporting the chirality effect in the second-order Raman spectra observed here. For MOD1 and MOD2 near-armchair semiconducting tubes such as (7, 5) and (7, 6), however, they display M band and iTOLA band with comparable intensities (Figure 7.1 for the spectra).

Because the M and iTOLA bands have similar resonance excitation profiles (Figure 7.4a, b), we believe the observed chirality effect is intrinsic and not due to the different resonance enhancement for these two bands. It is interesting to note that the chirality effect observed here is analogous to the chirality effect observed previously in a study of the dependence of SWNTs optical transition energies  $E_{ii}$  on incident laser power density on the sample.<sup>116</sup> The transition energies  $E_{ii}$  were found to undergo a downshift for MOD1 tubes and an upshift for MOD2 tubes, with the magnitude of variation in  $E_{ii}$  larger for near-zigzag tubes.<sup>116</sup> In the present work, opposite effects of tube chirality on the relative intensity of the M band and iTOLA band are observed for MOD1 and MOD2 semiconducting tubes. We expect that the trigonal warping effect<sup>53,74</sup> of the electronic and phonon structures of nanotubes may need to be considered in order to interpret this chirality effect observed in the present work.

#### 7.4. Temperature dependence and fine structures of second-order modes

We also performed low-temperature Raman spectroscopy on a few individual nanotubes to better resolve their second-order Raman features. Figure 7.5a compares the iTOLA band of the (13, 0) tube measured at 298 K and at nominal 5 K. The iTOLA band of this tube displays a steep lower-energy edge and a gradual tail at the

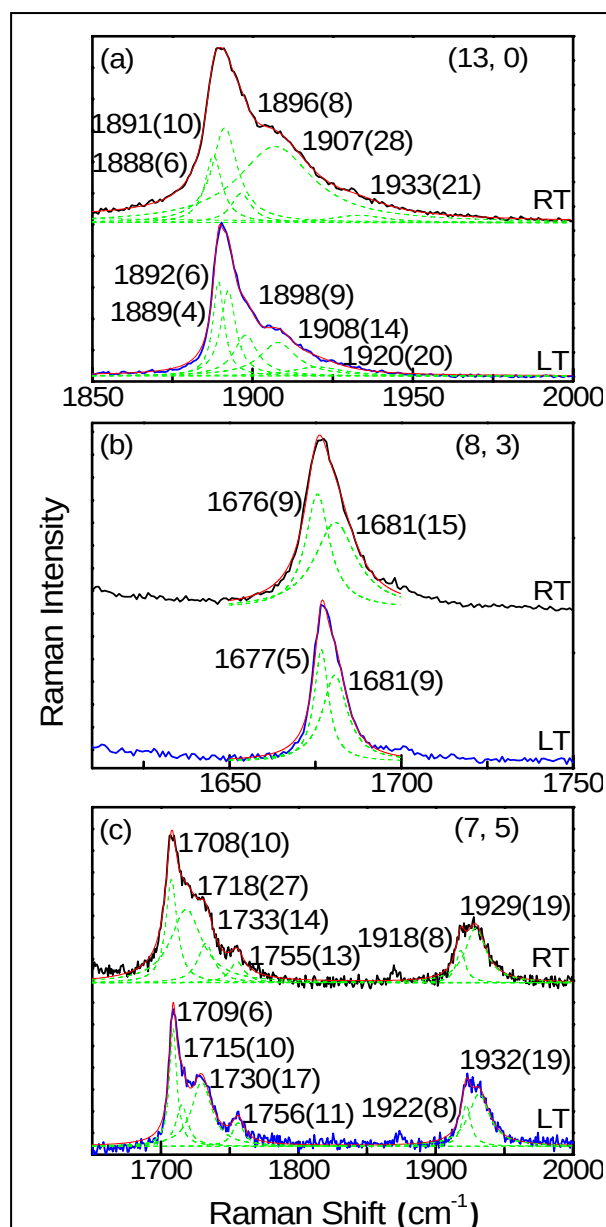


**Figure 7.5** Second-order Raman spectra of three individual semiconducting tubes acquired at room temperature 298 K (RT, black curves) and low temperature 10 K (LT, blue curves): (a) iTOLA band of a (13, 0) tube, (b) the M band of a (8, 3) tube, and (c) both the M band and iTOLA band of a (7, 5) tube. The spectra are fitted with a superposition of Lorentzian peaks (green curves), with fitted peak positions and line widths (FWHM, in parentheses) in  $\text{cm}^{-1}$  shown for each spectrum. The G band spectra of these tubes at RT are shown in Figure 7.1.

high-energy side. While the iTOLA band of bulk SWNTs was usually fitted by two peaks,<sup>157</sup> the same band of this single tube exhibits more fine features. Five Lorentzian lines (1 through 5 in the order of increasing frequency) are needed to fit the low-temperature spectrum satisfactorily: two lines (1 and 2) for the low-energy intense peak, two lines (3 and 4) for the high-energy broad feature, and one line (5) for the low-intensity tail. The room temperature spectrum is thus also fitted with five Lorentzian lines. When temperature is decreased from 298 to nominal 5 K, the  $G^+$  mode of this tube exhibited an upshift of  $\sim 2 \text{ cm}^{-1}$ , with its FWHM decreasing from 8 to 6  $\text{cm}^{-1}$ , which is shown in chapter 6. As expected, the line-narrowing behavior is also observed for the iTOLA band and is most significant for line 4, which has a FWHM of 14

$\text{cm}^{-1}$  at nominal 5 K compared to 28  $\text{cm}^{-1}$  at 298 K. Similar to the  $G^+$  mode, all lines

except the tail (line 5) of the iTOLA band slightly upshift by  $1\text{--}2\text{ cm}^{-1}$  when temperature is lowered to 5 K. In addition, the intensity of line 4, corresponding to the broad component at  $\sim 1907\text{ cm}^{-1}$ , becomes much weaker at the low temperature.

Figure 7.5b compares the M band spectra of a (8, 3) tube at 298 and 5 K. Both spectra appear slightly asymmetric and, as in the ensemble spectra, two Lorentzian lines are found to fit both spectra satisfactorily. As expected, the two Lorentzian lines become much narrower when temperature is lowered to 5 K. It can also be seen that the lower-energy line displays a slight upshift of  $\sim 1\text{ cm}^{-1}$ , while there is no observable variation for the higher-energy line when the temperature is decreased to 5 K.

We also measured the temperature dependent Raman spectra of a (7, 5) tube, which displays the M band and iTOLA band as shown in Figure 7.5c. Interestingly, its M band has a very asymmetric shape similar to the iTOLA band of the (13, 0) tube, and its iTOLA band appears similar in shape to the M band of the (8, 3) tube. Four and two Lorentzian lines are needed to fit the M band and iTOLA band spectra of this tube, respectively, as indicated in Figure 7.5c. As expected, most lines become narrower at lower temperature.

There is also a change in the intensity ratios  $I_{\text{iTOLA}}/I_{\text{G}}$  and  $I_{\text{M}}/I_{\text{G}}$  of single tubes when temperature is lowered, which is expected because of the temperature dependence of the electronic transition energy  $E_{\text{ii}}$  of SWNTs.<sup>116-118</sup> The ratio  $I_{\text{iTOLA}}/I_{\text{G}}$  of the (13, 0) tube in Figure 7.5a shows a decrease from 0.78 to 0.48, and the ratio  $I_{\text{M}}/I_{\text{G}}$  of the (8, 3) tube in Figure 7.5b also decreases from 0.19 to 0.13 when temperature is changed from 298 to nominal 5 K.

A more significant, temperature-induced change in the relative intensity of the M band is observed on a metallic tube, shown in Figure 7.6. This metallic tube has a RBM  $\sim 178\text{ cm}^{-1}$  and tentatively assigned to (14, 5) chirality. In this case, when

temperature is decreased from 298 to 5 K, the M band feature of this tube at  $\sim 1730 \text{ cm}^{-1}$  is enhanced by a factor of  $\sim 5$ , so that its peak intensity becomes stronger than the G band at the low temperature 5 K. This indicates that when temperature is changed to 5 K the exciton transition energy  $E_{ii}$  of this tube becomes closer to the resonance condition of M band, most likely the scattering photon resonance  $E_{ii} = E_{\text{laser}} - E_M$ .

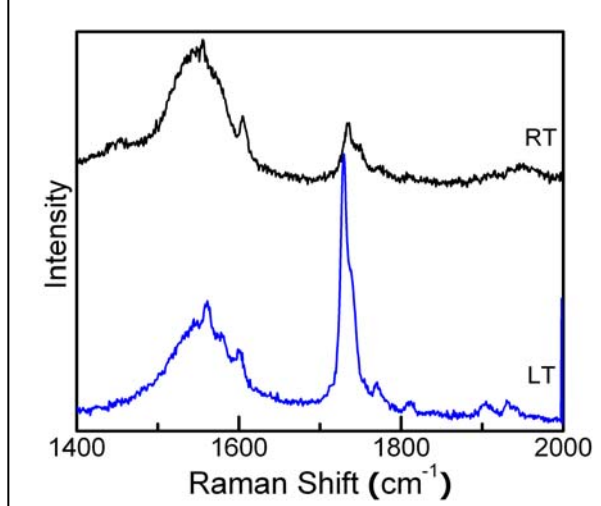


**Figure 7.6** The G band and second-order Raman spectra of a metallic tube, assigned to (14, 5), acquired at room temperature 298 K (RT, black curve) and low temperature 5 K (LT, blue curve). The LT spectrum shows an enhanced M band.

### 7.5. Implication to the assignment of the iTOLA Raman mode

The highly dispersive behavior of the iTOLA band observed in ensemble Raman measurement on SWNTs is generally explained by a double-resonance Raman scattering mechanism.<sup>35,159,160</sup> The same mechanism has been used to interpret the dispersive behavior of the D and G' modes in graphite materials. In the double-resonance process, either the initially created state or the final state of electrons and the phonon scattered intermediate state are actual electronic states.<sup>159</sup> The allowed double-resonance processes lead to selective excitation of phonons with  $|q| \cong 0$  and  $|q| \cong 2|k|$ , where  $k$  and  $q$  are the electron wave vector and phonon wave vector, respectively. The wave vectors  $|q| \cong 0$  do not depend on  $E_{\text{laser}}$ , while those  $|q| \cong 2|k|$  are sensitive to  $E_{\text{laser}}$  because of the  $k$  selection by varying  $E_{\text{laser}}$ . The independence of the iTOLA mode frequency of single tubes on excitation energy  $E_{\text{laser}}$  observed in the

present work suggests that the phonon wave vectors  $|q| \cong 0$  should be related to the iTOLA band. However, it is not expected to observe the iTOLA feature corresponding to  $|q| \cong 0$  in graphitic materials<sup>138,155</sup> because the LA mode frequency  $\omega_{\text{LA}} = 0$  and iTOLA frequency  $\omega_{\text{iTO}} = 1582 \text{ cm}^{-1}$  for  $|q| \cong 0$ . This should also hold true for SWNTs. At present, it is not clear why the iTOLA band of single tubes, which corresponds to  $|q| \cong 0$  as determined from excitation wavelength-dependent Raman measurements, can be observed. Future theoretical work is needed to account for the non-dispersive behavior of the iTOLA band in single tubes as well as their fine structure consisting of up to five peaks for some tubes.

## 7.6. Summary

Second-order Raman features between  $1650$  and  $2000 \text{ cm}^{-1}$  of single-wall carbon nanotubes, including G+RBM and iTOLA combination modes and the overtone M band, are studied using single nanotube Raman spectroscopy. The combination mode involving the G mode and RBM is clearly identified in small-diameter semiconducting tubes. Excitation wavelength-dependent Raman spectroscopy performed on single nanotubes reveals that the M band and iTOLA mode are nondispersive with respect to excitation energy, in contrast to the dispersive behavior observed in the ensemble measurement. Some unusual single tube Raman spectra with enhanced second-order modes are observed and are attributed to the resonance of scattered photons with exciton transitions of the nanotubes. It is also discovered that the relative intensity of the M band and iTOLA mode depends on the chiral structure and family type of a nanotube. Low-temperature Raman spectroscopy is used to better resolve the fine structures of second-order Raman spectra.

## Chapter 8

### Summary and conclusion

We have developed a beam-scanning confocal Raman microscope which is capable of imaging single nanotubes grown on a large substrate surface. By using this system, we imaged and characterized ultra long SWNTs grown on Si substrate by the CVD method. The vibrational, structural and electronic properties of nanotubes are studied by our Raman imaging and spectroscopy. A large variation in the RBM intensity for different nanotubes is observed, which can be ascribed to difference extent of resonance enhancement and also the structure dependence of electron-phonon coupling elements. We also observe very different line shapes of G band Raman spectra (BWF feature) of metallic nanotubes compared to semiconducting tubes. The BWF feature is found to be diminished in most of isolated metallic tubes in air, which is most likely caused by unintentional charge doping due to O<sub>2</sub> adsorption.

The charge doping dependence of G band Raman spectra of metallic tubes is further studied by both electrostatic gating and electrochemical gating. In electrostatic doping experiment, significant irreversible changes are observed for metallic nanotubes exposed to ambient air, suggesting a strong doping dependent electron-phonon interaction. The magnitude of the doping dependent LO mode shift and change in the line width are found to be larger than that of the previous similar studies carried out in vacuum. Also a significant hysteresis behavior is observed. We attribute these behaviors to the trapping of negative charges on SiO<sub>2</sub> surface around the nanotubes, which is believed to be assisted and stabilized by water adsorption. The smooth gradual change of G band spectrum from semiconducting-type to the broad BWF type provide preliminary evidence of LO-TO phonon interaction when they

have same frequency. As a more reproducible alternative, electrochemical doping experiment allows to observe reversible changes of G band spectra of several metallic and semiconducting tubes. The doping dependent G band spectral change of metallic tubes is consistent with the results in electrostatic doping experiment. However, the chemical reaction between the electrolyte polymer solution and metal electrodes limited the magnitude of voltage applied to the tubes. The electrochemical stability of the electrolyte solution needs to be further improved by, for example, removing oxygen and water from the system.

We studied Raman spectra of 12 individual nanotubes with different diameter at both room temperature 295 K and low temperature 5 K, and Raman spectra of single-layer graphene over a temperature range from 295 K to 5 K. The temperature-induced G band Raman frequency shift is found to be tube diameter dependent, which can be explained by the fact that the nanotube curvature will affect the temperature dependence of C–C bond force constants in SWNTs. However, the diameter dependence of temperature-induced RBM frequency changes is mainly attributed to the temperature dependent tube-substrate interaction. The  $G^-$  BWF peak of different individual metallic tubes shows different temperature dependence. It can be explained by the different degree of charge doping that will affect Kohn anomaly mechanism. This observation gives preview of a future direction that studies the doping dependence of metallic nanotubes at low temperature.

Finally, second-order Raman features between  $1650$  and  $2000\text{ cm}^{-1}$ , including overtone M band, and G+RBM and iTOLA combination modes, are studied for some small-diameter individual SWNTs. Excitation wavelength-dependent Raman spectroscopy reveals the M band and iTOLA modes are non-dispersive to excitation energy. It is also found the second-order modes can be enhanced when the scattered

photons are in resonance with exciton transitions of the nanotube. The relative intensity of M band and iTOLA is found to depend on the chirality of nanotubes, which is probably related to the trigonal warping effect. Low temperature Raman spectroscopy is also carried out to provide fine structures of second-order Raman spectra. The observed characteristics of second-order Raman modes provide additional useful information on the chirality and electronic structures of carbon nanotubes. The present work renders it necessary to reconsider the double-resonance Raman theory in order to account for the non-dispersive behavior of these second-order Raman modes in single tubes as well as their fine structures consisting of multiple peaks.

## Publications

L. Zhang, L. Huang, M. Lind, V. Liao, S. O'Brien, and Z. Yu,

“Excitation, temperature, and structural dependence of second-order Raman modes in single-wall carbon nanotubes”, *J. Phys. Chem. C* **2009**, 113, 16432

L. Zhang, L. Huang, S. P. O'Brien and Z. Yu,

“Electrostatic doping-induced phonon shift of metallic single-wall carbon nanotubes”, *J. Phys. Chem. C* **2008**, 112, 20118

L. Zhang, Z. Jia, L. Huang, S. P. O'Brien and Z. Yu,

“Low-temperature Raman spectroscopy of individual single-wall carbon nanotubes and single-layer graphene”, *J. Phys. Chem. C* **2008**, 112, 13893

L. Zhang, S. Aite and Z. Yu,

“Unique laser-scanning optical microscope for low-temperature imaging and spectroscopy”, *Rev. sci. instrum.* **2007**, 78, 083701.

L. Zhang, Z. Jia, L. Huang, S. P. O'Brien and Z. Yu,

“Imaging and Raman spectroscopy of individual single-wall carbon nanotubes on a large substrate”, *J. Phys. Chem. C* **2007**, 111, 11240.

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“Imaging and Raman spectroscopy of individual single-wall carbon nanotubes at room temp and low temp”, *Frontiers of Nanotechnology & Biotechnology Integration and Invention* 2008, Conference Poster

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“Raman imaging and spectroscopy of individual carbon nanotubes”, *Junior Scientist Conference* 2006, Conference Poster

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