

CHARGING AND DEFECTS IN SINGLE-WALLED CARBON NANOTUBES

BY

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DISSERTATION

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ABSTRACT

Single-Walled Carbon Nanotubes (SWCNTs) have been one of the most intensively studied materials. Because of their single-atomic-layer structure, SWCNTs are extremely sensitive to environmental interactions, in which charge transfer and defect formation are the most notable effects. Among a number of microscopic and spectroscopic methods, Raman spectroscopy is a widely used technique to characterize physics and chemistry of CNTs. By utilizing simultaneous Raman and electron transport measurements along with polymer electrolyte gating, this dissertation focuses on studying charging and defects in SWCNTs at single nanotube level and in single layer graphene, the building block of SWCNTs.

By controllably charging metallic SWCNTs (m-CNTs), the intrinsic nature of the broad and asymmetric Fano lineshape in Raman G band of m-CNTs was first time evidenced. The observation that Fano component is most broadened and downshifted when Fermi level is close to the Dirac point (DP) reveals its origin as the consequence of coupling of phonon to vertical electronic transitions. Furthermore, we have systematically introduced covalent defects to m-CNTs to study how phonon softening and electrical characteristics are affected by disorders. In addition to decreasing electrical conductance with increasing on/off current ratio eventually leading to semiconducting behavior, adding covalent defects reduces the degree of softening and broadening of longitudinal optical (LO) phonon mode but enhances the softening of transverse optical (TO) mode of the G-band near the DP. Charging and defect effects in semiconducting SWCNTs and single layer graphene, a closely related material to SWCNTs, have also been discussed.

To my Mother

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Ken and Mary Jo Rott have been constant source of encouragement to me. They are like my spiritual grandparents who keep my belief in kindness and love. I am indebted to them for making a home away from home for me.

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CHAPTER 1

CARBON NANOTUBES BASICS, SYNTHESIS, AND METROLOGY

1.1. Introduction

Since their discovery in 1991, carbon nanotubes (CNTs) have been one of the most intensively studied materials and have kept intriguing both scientists and engineers in the last two decades. The number of publications on CNTs keeps increasing as shown in figure 1.1 [1] and it sets CNTs apart from other research areas that appear ideal at the beginning, for example, high temperature superconductivity. The reason for that unusual continuing vitality is the unique combination of exceptional properties of CNTs. First, CNTs are two order of magnitude stronger than steel at 1/6th of the weight. CNTs are also excellent conductors of heat [2]. Moreover, CNTs offer extremely high carrier mobility, up to 10^5 cm²/V.s, two orders of magnitude higher than current silicon electronics. In addition, CNTs appear to be biocompatible in many environments [3].

Thanks to an amazing combination of properties, CNTs appear to be ideal for a wide range of applications, including molecular electronics, quantum computing, materials science, and medicine. Electronic applications of CNTs grab most of media limelight because of the thrust for smaller and faster devices. Electron-phonon coupling is particularly important for transport properties in CNTs, as it is ultimate limiting factor of high-field carrier mobility [4, 5, 6]. Therefore, electron-phonon coupling, which can be quantified via phonon frequency, linewidth, and intensity measured by Raman spectroscopy, is important to understand for both CNT applications and fundamental sciences. This thesis focuses on studying electron-phonon coupling in single-walled

CNTs (SWCNTs) under charging and defects by utilizing simultaneous Raman and transport measurements, and polymer electrolyte gating.

SWCNTs can be considered as one atom thick graphene sheet rolled up into seamless tubes, one atom thick, along chiral vector C_h , as indicated in figure 1.2. Chiral vector is described by $C_h = na_1 + ma_2$ where a_1 and a_2 are unit vectors of the hexagonal lattice; n and m are integer, $0 \leq m \leq n$, and are called chiral indices. Each SWCNT is characterized by a pair of n and m , as (n,m) . They are called armchair if $m=n$, zigzag if $m=0$, and chiral nanotubes in all other cases.

The electronic properties of SWCNTs depend on n and m . They are metallic nanotubes (m-CNTs) if the difference between n and m is a multiple of three (though only armchair nanotubes are truly metallic) and semiconducting nanotubes (s-CNTs) otherwise [2]. For m-CNTs, the valence and conduction bands touch each other at a single point, Dirac point (DP), as shown in figure 1.3b, which is not the case for s-CNTs where a diameter dependent bandgap of about 0.5 eV is formed as indicated in figure 1.3a. Of particular interest is the density of states (DOS) of SWCNTs with the appearance of van Hove singularities (vHs) as expected for 1D materials. A finite DOS between the first two vHs of m-CNTs distinguishes them from s-CNTs (figures 1.3c and 1.3d). These characteristics play a crucial role in understanding many physical as well as chemical properties of CNTs, and some of them will be described in the following.

1.2. Single-Walled Carbon Nanotube Metrology

The existence of SWCNTs and their properties are evidenced and investigated by several techniques, for instance, electron microscopy, scanning probe microscopy, and optical techniques. While each method has both advantages and disadvantages,

combinations of techniques give us a comprehensive picture of SWCNT characteristics and potential applications. Methods that are used to characterize SWCNTs in this work are briefly summarized below.

1.2.1. Atomic Force Microscopy

In atomic force microscopy (AFM), a sharp tip in the shape of a pyramid moves over the contours of the surface, at near-atomic precision, and as it does so, the cantilever at the back of the tip moves up and down. This motion is detected using the deflection of a laser beam, which bounces off the back of the cantilever, and thus a map of any surface is obtained, at a resolution of less than 1nm vertically. There are different modes - contact mode, in which the tip is scraping across the surface, noncontact mode or tapping mode, in which the tip vibrates up and down, and responds to the proximity of the surface, without actually touching it, and ultrasonic mode, or UFM, in which the sample is vibrated at very high frequencies (1-2 MHz), which causes the tip to sense the relative softness of various features on the surface in addition to a high resolution. In our work, we use tapping mode to image CNTs on silicon substrate with 300 nm thick SiO₂ oxide layer in order to check the number of CNTs in the channel of devices and to see if tube of interest are isolated as well as nanotube diameter. An AFM image of a single connection CNT-based FET is shown in figure 1.12.

1.2.2. Electrical Measurement

Electrical measurements of individual SWCNTs have proven to be a powerful probe of this novel 1D system. Figure 1.4 shows a schematic of commonly used device geometry. A SWCNT is connected to two metallic contacts, source and drain electrodes,

and capacitively coupled to the third electrode that is used to change charge density, or, in other words, control the Fermi level, in the SWCNT. This three-terminal geometry has been used to address both device performance and fundamental physics [7].

The transport properties of SWCNTs are directly related to their electronic structure. Transconductance measurement is a means to distinguish s-CNTs and m-CNTs as indicated in figure 1.5. Semiconducting SWCNT exhibits a broad range of zero-conductance because of Fermi level tuned into bandgap while m-CNT shows slight gate dependence as Fermi level reaches the first vHs. Conductance depends also on contact resistance and carrier scattering rate. For the former, Au and Pd have proven to make the best contacts (Ohmic) to CNTs with nearly perfect transmission [8]. For the latter, defect scattering and electron-phonon coupling are dominant mechanisms [4, 5, 6, 9, 10]

There are several sources of disorders in CNTs. The first one is localized lattice defects, such as vacancies, substitutions, and pentagon-heptagon defects. Such defects are typically formed during nanotube growth or by intentional damage [9]. The second source is electrostatic potential fluctuations, created by contaminants or trapped charges in the substrate, or by adsorbed molecules. The third one is mechanical deformations, for instance, strain, twist and kinks [10]. The presence of these defects reduces the transmission coefficient of carrier transport [9, 10].

In clean, high-quality m-CNTs at room temperature, the dominant scattering mechanism is well known to be electron-phonon scattering [4, 5, 6, 11]. Scattering by acoustic phonons dominates the resistance at low source-drain bias [11], whereas scattering by optical and zone boundary phonons sets a limit on maximum current carried out by individual CNT at high bias [4, 5, 6]. The latter is shown in figure 1.6 for a m-

CNT. The slope of current-voltage curve decreases for increasing bias, and can even become negative for suspended CNT. This is explained by phonon emission by electrons as soon as they gain energy equal to optical phonon energy, $\sim 0.16\text{eV}$. The energy created by phonon emission can heat CNT significantly, particularly for suspended tubes, which are not supported by substrate for heat dissipation, and can lead to negative differential resistance [12].

Phonon scattering also limit the ultimate performance of s-CNT devices as shown in figure 1.7 for temperature dependence of the linear conductance of such a device [13]. The on-state resistance increases linearly with temperature, indicative of scattering by acoustic phonons, whose occupation also grows linearly with temperature.

1.2.3. Raman Spectroscopy

Raman spectroscopy is one of the most sensitive, easy-to-use, and powerful techniques in characterizing CNTs. It can be performed on both bundled and single CNTs, and carried out at room temperature and ambient pressure. Raman spectroscopy has been used to characterize SWCNTs for many different purposes, from synthesis and purification process all the way to nanotube modifications and device applications. This section presents an overview of Raman spectroscopy in SWCNTs.

Raman scattering is an inelastic scattering of photons. Through phonon excitation (or relaxation), scattered photon loses (or gains) the characteristic energy of phonon relative to energy of incident photon. A schematic Raman scattering is shown in figure 1.8. Raman spectra refer to the spectral intensity of scattered photon as a function of energy shift, or phonon energy. The photon scattering process generally occurs even without support of electronic structure which would correspond to a nonresonant process

with weak Raman signal. However, thanks to the resonance of incident or scattered photons with an optical transition between vHs (e.g., E_{11} as shown in figure 1.3d) of this 1-D material, scattering amplitude becomes large, and makes the observation of Raman signal from CNTs at single tube level possible. Figure 1.9 gives examples of Raman spectra from an individual CNT with four prominent features: Radial breathing mode (RBM), defect-related D-band and its overtone 2D band, and tangential mode (or G-band). The importance of these Raman modes is discussed in detail below.

- ***Radial Breathing Mode (RBM)***

RBM is one signature that distinguishes CNT from other forms of graphitic materials. RBM corresponds to the symmetric in-phase displacements of all carbon atoms in CNT in the radial direction, with frequency in the range $100\text{-}350\text{ cm}^{-1}$. As expected, RBM frequency is proportional to reciprocal of nanotube diameter [14] and usually used to determine nanotube chirality as indicated in figure 1.10, the Kataura plot. Each point corresponds to an optical transition with a specific chirality (n, m) [15, 16]. Since Kataura plot is based on one electron electronic structure which does not take into account electron-electron interaction, electron-phonon interaction, or interaction between CNT and its surroundings, the plot can serve as a rough reference.

- ***Tangential Mode***

The multiple-feature Raman G-band is another important characteristic of CNTs. The optical phonon G mode arises from the tangential vibration of carbon atoms in the range $1500\text{-}1630\text{ cm}^{-1}$. It corresponds to the in-plane E_{2g} optical phonon mode in the parent graphene. Since unit cell of graphene consists of two equivalent atoms, the

longitudinal (LO) and transverse (TO) optical modes are degenerate at zone center of the Brillouin zone. When graphene is rolled up to form a SWCNT, due to the radial confinement and curvature of cylindrical shape, the degeneracy is removed, and G-band mainly splits into two features, G^+ and G^- , in which G^- mode has lower frequency. For s-CNTs, G^+ corresponds to the LO mode, and G^- to the TO mode, which is softened due to the mixing of sp^2 and sp^3 bond characteristics induced by curvature effects [17] Both narrow and symmetric G^+ and G^- peaks can be well fitted by Lorentzian function. For m-CNTs, while G^+ has narrow Lorentzian lineshape G^- shows either Lorentzian or asymmetric and broad Fano lineshape which is represented by Breit-Wigner-Fano line shape: $I(\omega) = I_0 \frac{[1 + (\omega - \omega_0)/q\Gamma]^2}{1 + [(\omega - \omega_0)/\Gamma]^2}$ where ω_0 , I_0 and Γ is frequency, intensity, and

broadening parameter, respectively, $1/q$ is a measure of the interaction of phonon with a continuum of states [18] These have been debates in whether Fano lineshape is intrinsic property of metallic NTs [19] or arising from bundle effect [20], whether it is TO [22] or LO [21, 22, 23] mode, and whether it is caused by electron-plasmon coupling [22] or special electron-phonon coupling (i.e. Kohn anomaly in which phonon energy decreases abruptly due to the change in the screening of atomic vibrations by conduction electrons) [25, 24]. The picture of G^+ component is also not simple. While some reports show that G^+ frequency should be independent of charge transfer [25, 26], some indicate that it stiffens [27, 28], and other states that both trends can be observed [29] These discrepancies are subjects of chapters 3 and 4. The sensitivity of Raman G-band in s-CNTs to doping and defects formation will be discussed in chapter 5.

- ***D band and 2D band***

In addition to RBM and G-band, D-band and 2D band can be observed in Raman spectra as shown in figure 1.9. Centered around 1320cm^{-1} , D-band originates from disorder-assisted double resonance process [30], involving a single phonon scattering and a defect scattering (figure 1.8). The integrated intensity D/G ratio is usually utilized to indicate the degree of defect [31]. The 2D peak, which involves two inelastic scattering events by two phonons with opposite wave vectors, is the second order of D peak and is measurable without the presence of defects [32]. The shape of 2D band can be used to identify charged defects in SWCNTs [33] since 2D band phonon energy renormalizes near charged defects, hence, inducing the appearance of an additional peak with frequency different for positive and negative charged defects. The shape of 2D band can also be utilized to characterize the number of layers of graphene because graphene layers have different electronic structures which create different numbers of peaks in 2D band [34].

1.3. Synthesis, Field Effect Transistor Fabrication and Characterization

There are several methods to produce CNTs. Historically, CNTs were first synthesized during an arc discharge between two graphite electrodes and by laser ablation of a graphite target. Both methods involve the condensation of hot gaseous carbon atoms generated from the evaporation of solid carbon with addition of metal catalyst. Only powdered samples in which CNTs are entangled in bundles are synthesized by arc discharge and laser ablation.

CVD method offers a more convenient way to integrate CNTs into electronic devices and to study this material at single SWCNT level. It involves the decomposition of a gaseous or volatile compound(s) of carbon, catalyzed by metallic particles, which

also serve as nucleation sites for the initiation of CNT growth. For our purposes, prior to CVD growth, catalyst islands are patterned by conventional photolithography on heavily doped Si/SiO₂ substrate with 300 nm thick oxide layer. Ferritin (Sigma-Aldrich, diluted 1000 times in DI water) catalyst is spin-coated on surface of substrate and then calcined at 800°C in air to remove organics. The sample is then heated up in a furnace to 900°C in H₂ with 200 cm³/min flow rate. CNT growth takes place by flowing methane as a carbon feedstock with ratio CH₄:H₂ = 300 cm³/min: 150 cm³/min for 15 minutes. The sample is then cooled down to less than 100°C under Ar (300 cm³/min) and H₂ (150 cm³/min) before being taken out for device fabrication.

After CNT growth, devices are fabricated by conventional optical lithography such that electrode and catalyst island patterns are aligned. Au electrodes (35nm) with Ti wetting layer (3nm) are deposited by e-beam evaporation. For all samples used here, the distance between source and drain electrodes is 4 µm. The device can be gated by a polymer electrolyte solution since polymer electrolytes provide nearly ideal gate efficiency for carrier injection in single CNT based FETs [35] Moreover, polymer electrolyte gating reduces hysteresis significantly and the short Debye length (~1 nm) of electrolyte solution can screen out many external effects, e.g. unexpected charging from the surroundings.

Electrochemical gate potential is applied with a nearby electrode, through a 20 wt% LiClO₄·3H₂O in polyethylenimine (Aldrich, low molecular weight) spin coated on top of electrically contacted SWCNTs. Thin polymer electrolyte film does not absorb in the wavelength of incident laser. The use of polymer electrolyte as gate medium allows

low voltage operation and electrical stability necessary for combined electrical and Raman measurements.

Raman measurements described throughout this thesis have been carried out on a JY LabRam HR 800 using a 1.96 eV excitation source through a 100x air objective (laser spot size $\sim 1\text{ }\mu\text{m}$). Laser power is kept at or below $\sim 1\text{ mW}$. Baseline correction is carried out by subtracting a spectrum collected $\sim 2\text{ }\mu\text{m}$ away from where the nanotube is located. Prior to electrical and Raman measurements, devices are imaged by AFM. AFM measurements are performed on Digital Instruments Dimension 3100 at low scan rate (1Hz).

A schematic of synthesis, fabrication, and characterization processes is shown in figure 1.11. An AFM image of one of the devices studied is also shown in figure 1.12 which exhibits a single CNT growing from one catalyst island to the other, across the channel, and connecting source and drain contacts.

In summary, the dependence of electronic properties on structure combined with the strong coupling of electrons and phonons in SWCNTs makes transport measurement and Raman spectroscopy very powerful characterization techniques in this field. The combination of these two methods can provide new insights on various crucial questions of CNT research, for example, the break down of Born-Openheimer approximation in CNTs [25, 36, 37, 38]. Taking advantages of simultaneous Raman and electrical measurements, this thesis is dedicated to studying charging and defects at the single SWCNT level. Specifically, chapters 2 and 3 discuss tunable electron-phonon coupling and influences of covalent defects in m-CNTs. Chapter 4 demonstrates the charging and

defect effects in s-CNTs. Chapter 5 is devoted to discuss these effects in graphene, the building block of SWCNTs.

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1.5. Figures

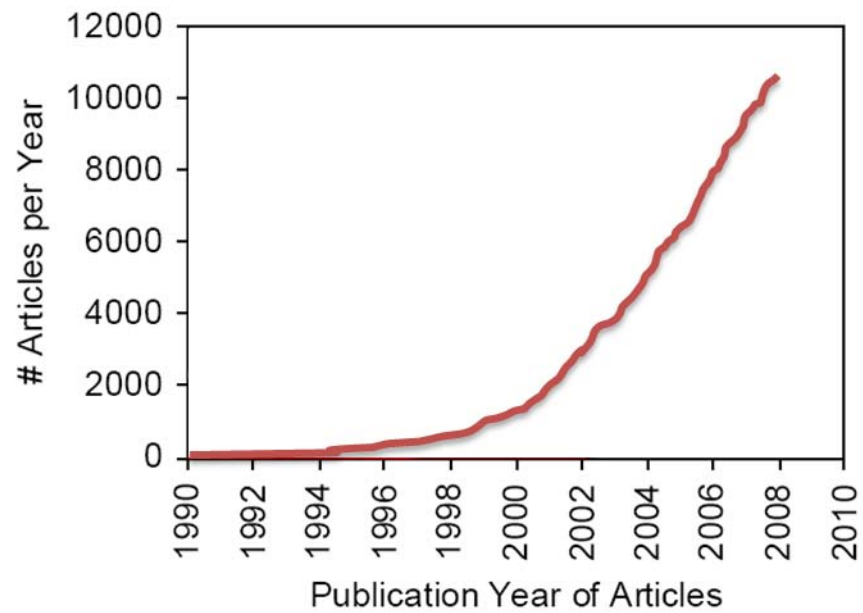


Figure 1.1: The rate of publications on carbon nanotubes (CNTs) continues to increase over the last two decades [1], indicating the unusual continuing vitality of CNTs.

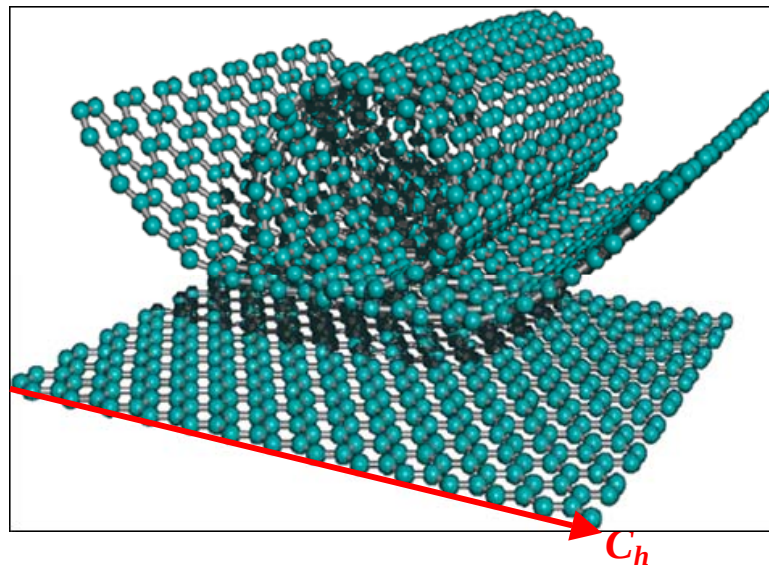
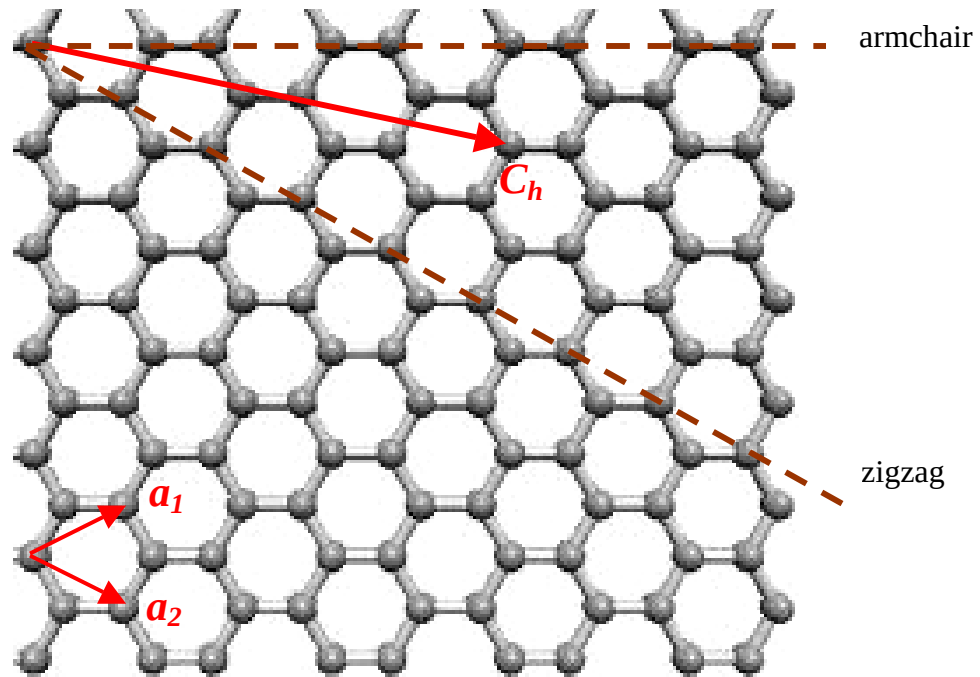


Figure 1.2: A graphene sheet (upper) is rolled up to create a SWCNTs (lower) with chiral vector $C_h = na_1 + ma_2$ in which a_1 and a_2 are unit vectors of the hexagonal lattice, n and m are integer and are called chiral indices of SWCNTs [2].

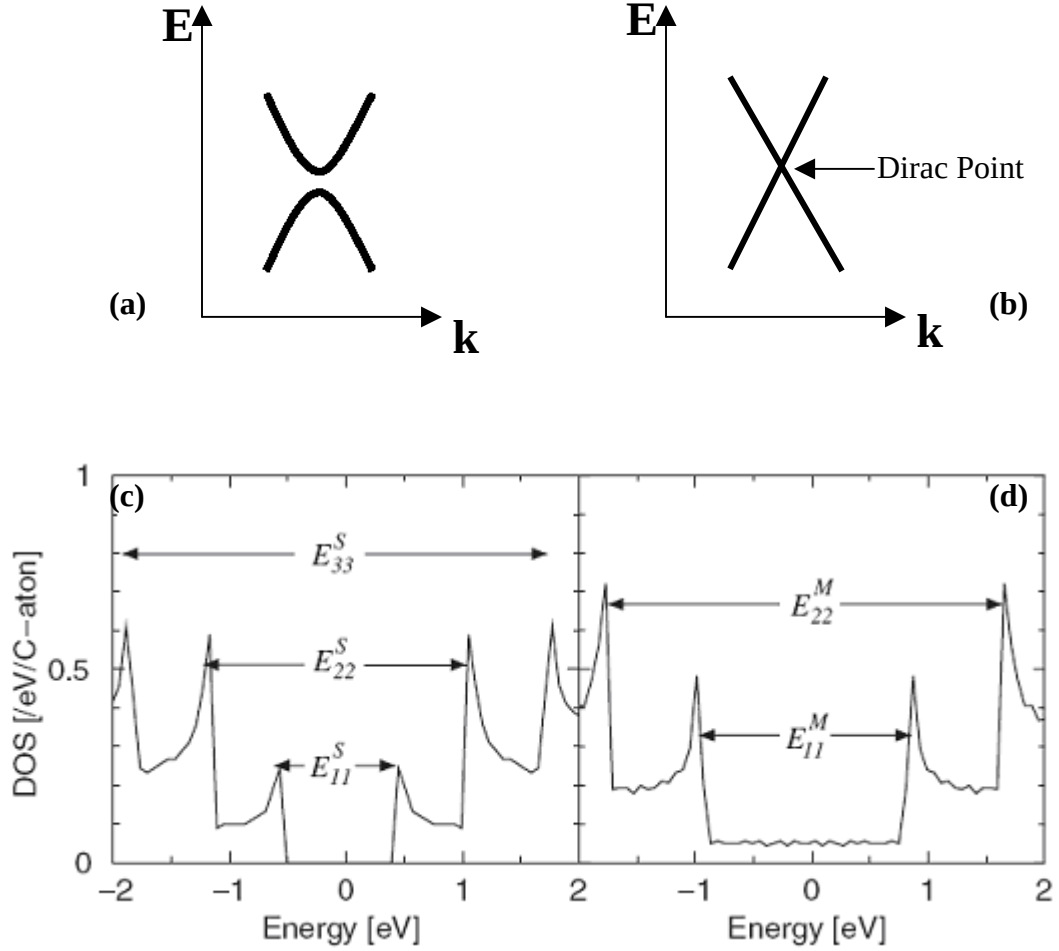


Figure 1.3: $E(k)$ diagram and density of states for s-CNTs (a and c, respectively) and m-CNTs (b and d, respectively) [2]. For m-CNTs, the valence and conduction bands touch each other at the Dirac point (DP), which is not in the case of s-CNTs where a diameter dependent bandgap of about 0.5 eV is formed. In addition, a finite DOS between the first two vHs of m-CNTs distinguishes themselves from s-CNTs as seen in figures 1.3c and 1.3d.

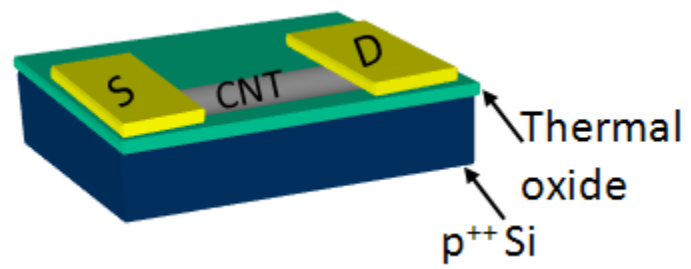


Figure 1.4: A schematic view of commonly used CNT-based FET geometry with Source (S), Drain (D) contacts, and heavily doped silicon served as a Gate.

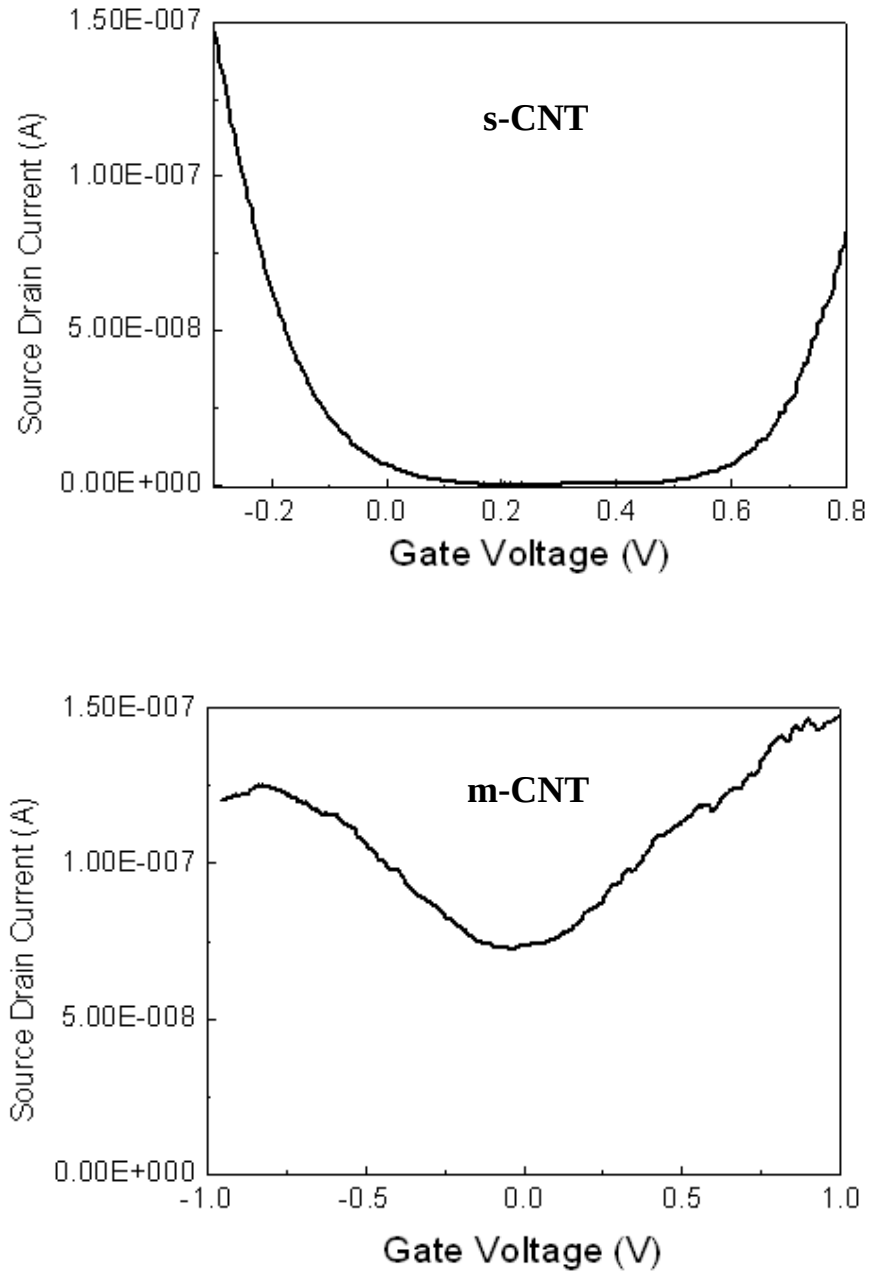


Figure 1.5: Transfer characteristic of a s-CNT (upper) and a m-CNT (lower). S-CNT exhibits a broad range of zero-conductance because of Fermi level tuned into bandgap while m-CNT shows only a moderate dip. Transfer characteristic is a means to distinguish s-CNTs and m-CNTs.

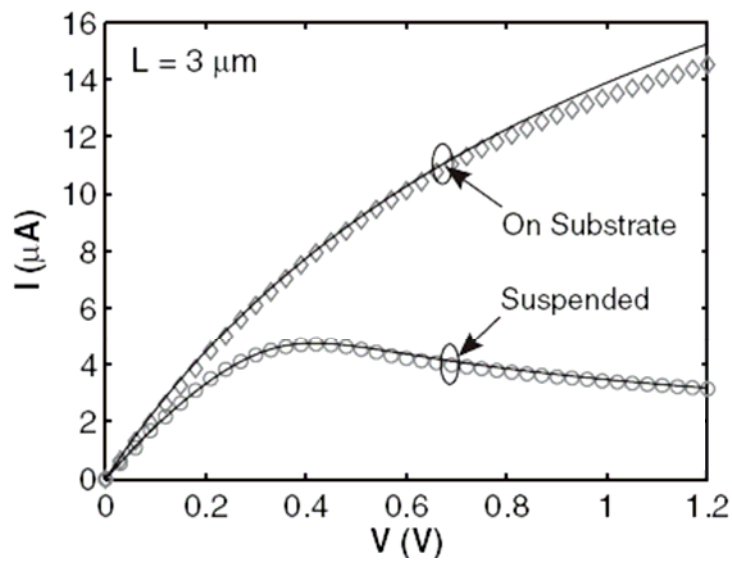


Figure 1.6: I-V characteristic of on-substrate and suspended parts of a m-CNT. The slope of current-voltage curve decreases for increasing bias, and can even become negative for suspended SWCNT. Scattering by optical and zone boundary phonons sets a limit on maximum current carried out by individual SWCNT at high bias [4, 5, 6].

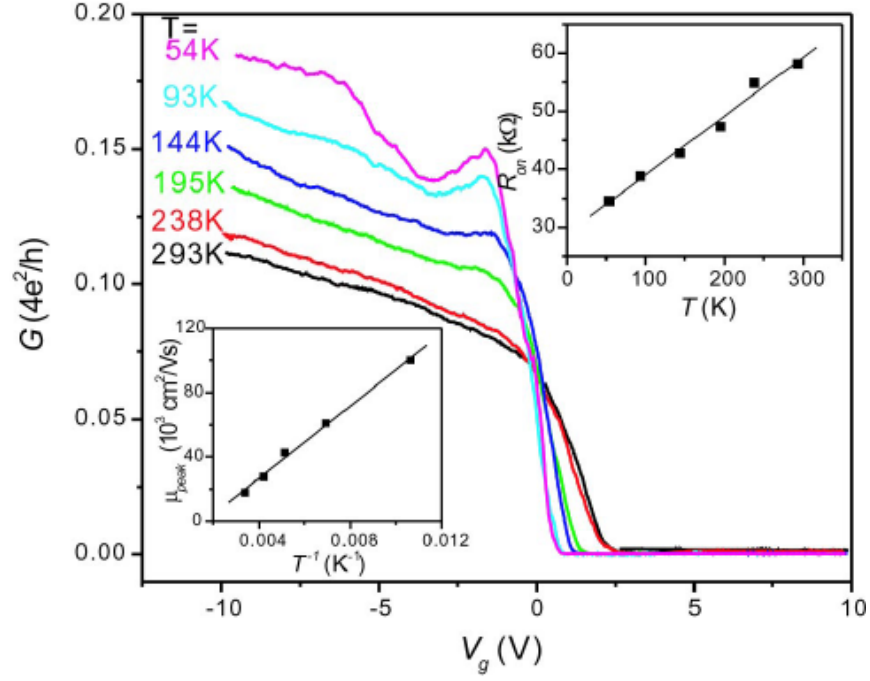


Figure 1.7: Conductance and mobility of a p-type semiconducting nanotube transistor vs. temperature. *Main figure:* The conductance vs. gate voltage at different temperatures. *Upper inset:* onset resistance, R_{on} , as a function of T . *Lower inset:* measured peak mobility as a function of T^{-1} . Both are shown with linear fitting [14]. The on-state resistance increases linearly with temperature, indicative of scattering by acoustic phonons, whose occupation also grows linearly with temperature.

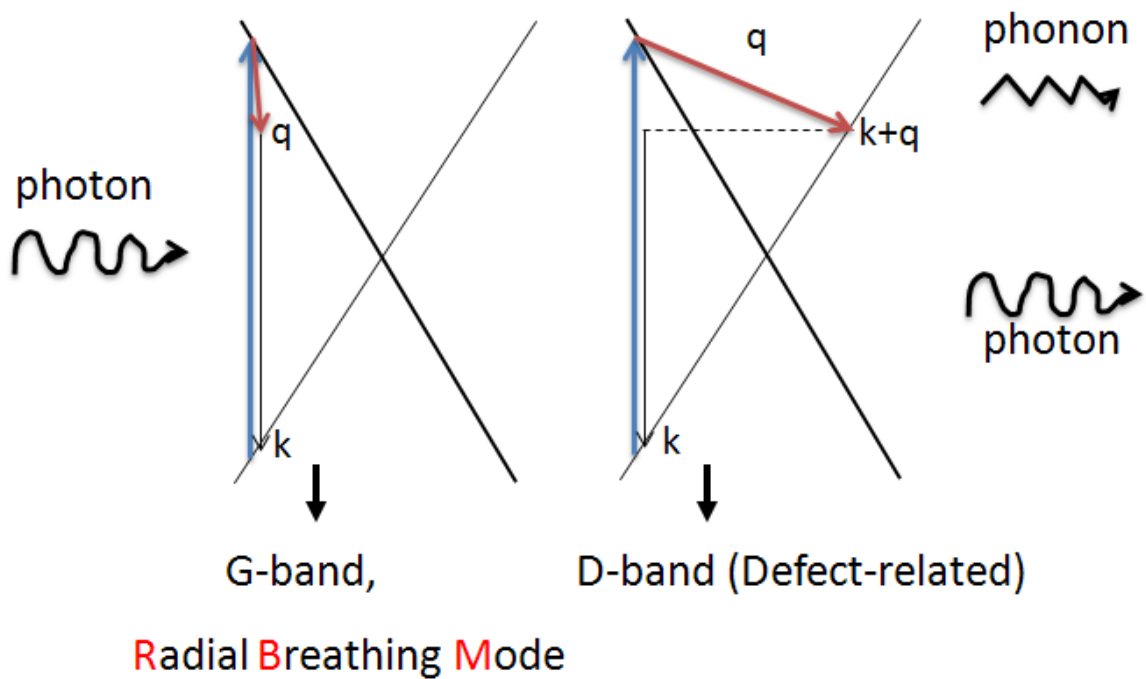


Figure 1.8: Incident photon resonance Raman scattering processes. A photon which matches with an electronic transition at wave vector k (thick arrow) gets scattered by a phonon with wave vector q , then relaxes (thin arrow). If $q \sim 0$, the scattering process gives rise to Radial Breathing Mode (RBM) and tangential mode (G-band) features, otherwise it involves elastic scattering (dashed line) with momentum conservation provided by a defect and gives rise to D-band feature.

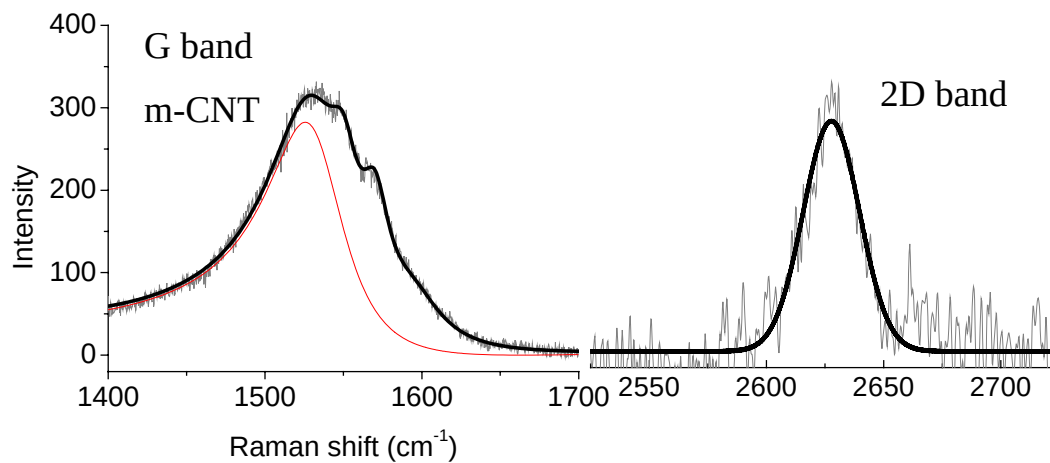
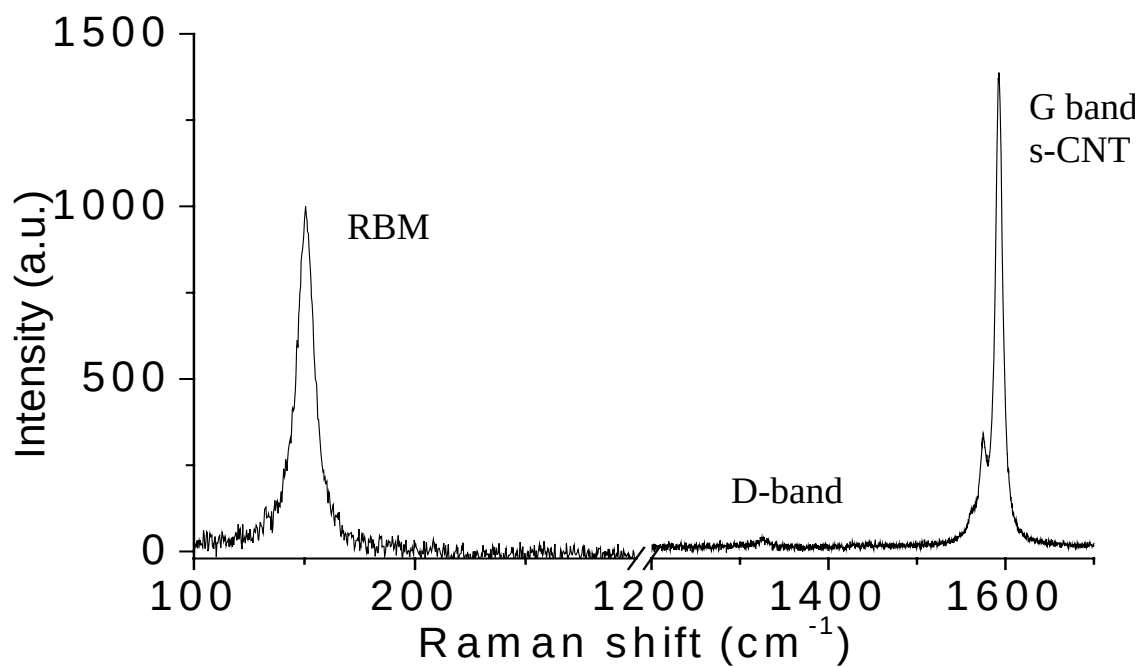


Figure 1.9: Raman spectrum with three main features: RBM, D-band, and G-band for a s-CNT (upper) and a m-CNT (lower) with broad and asymmetric Fano lineshape (thin line).

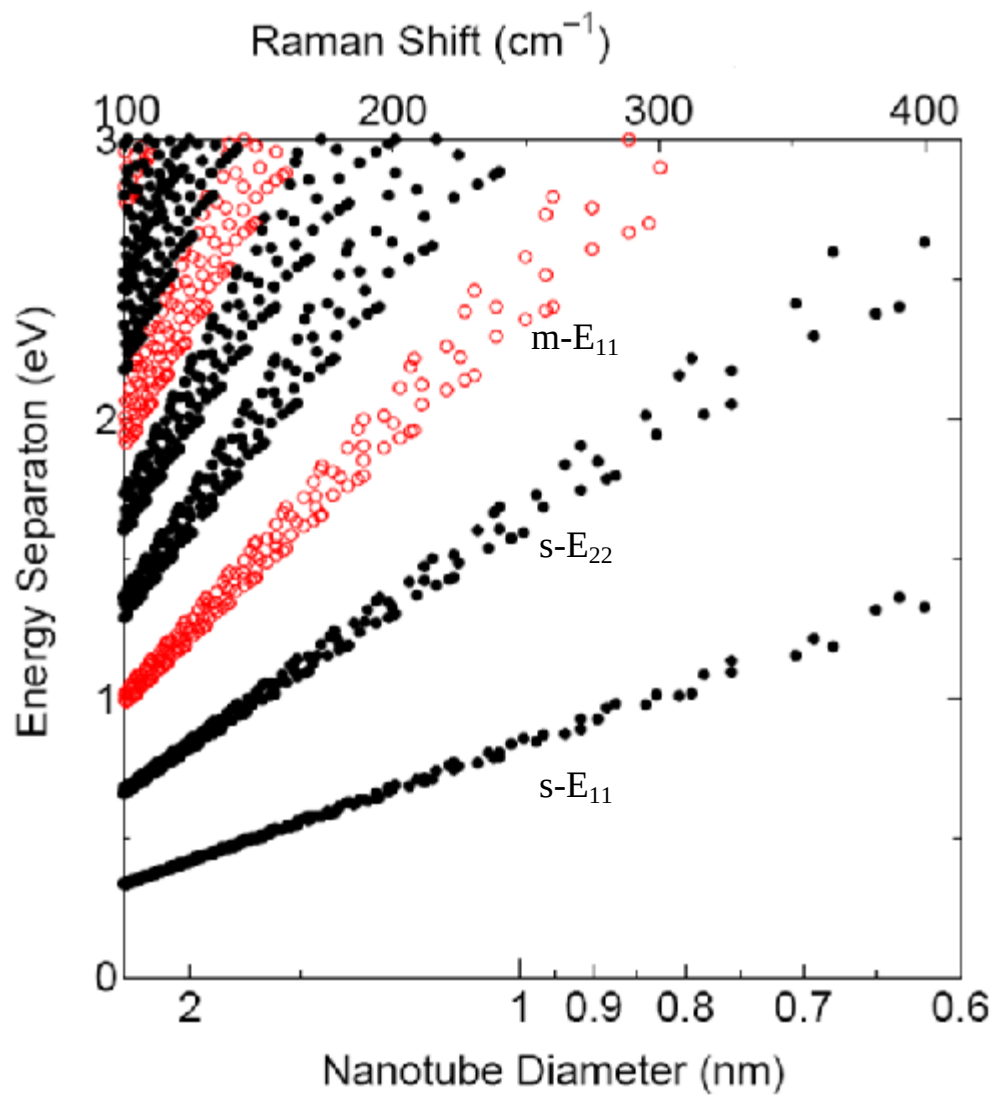


Figure 1.10: Kataura plot in which each point corresponds to specific electronic transition energy E_{ii} , nanotube diameter, and RBM frequency [15].

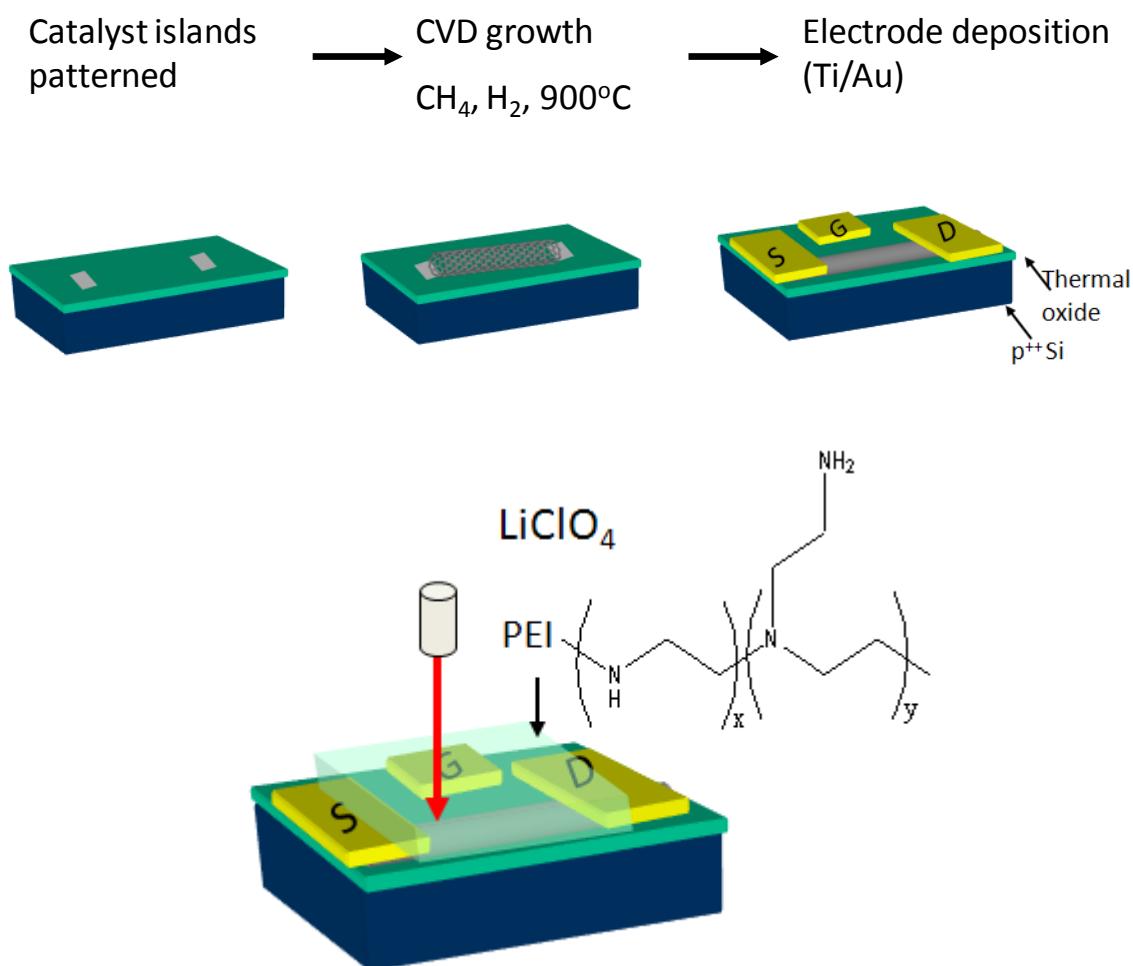


Figure 1.11: Schematic of CNT synthesis, CNT-FET fabrication, and simultaneous Raman and transport measurements with polymer electrolyte top gating.



Figure 1.12: An AFM image of a single connection CNT-based FET.

CHAPTER 2

CHARGING TO ELUCIDATE ELECTRON-PHONON COUPLING IN METALLIC CARBON NANOTUBES

Significant part of this chapter has been published as “Fano Lineshape and Phonon Softening in Single Isolated Metallic Carbon Nanotubes,” K. T. Nguyen, A. Gaur, and M. Shim, *Physical Review Letters* **98**, 145504 (2007).

2.1. Introduction

Electron-phonon interaction is critical for several important properties of CNTs, including electrical transport [1, 2, 3, 4], superconductivity [5], and optical transitions [6, 7]. The interaction between electrons and phonons is also important in Raman scattering, affecting Raman intensity, frequency, and linewidth. In turn, inelastic scattering can measure electron-phonon coupling [8, 9]. In this chapter, we will consider the optical phonon-electron interaction as it gives rise to a striking difference between G band feature of semiconducting and metallic SWCNTs.

Among various Raman features of SWCNTs, the broad and asymmetric Fano lineshape has received much attention. Conflicting reports exist on the presence of the broad downshifted G^- peak in isolated versus bundled m-CNTs. Initially, this feature has been attributed to phonon-plasmon coupling based on ensemble measurements [10]. Increasing linewidth and frequency downshift with decreasing average diameter have appeared consistent with the assignment of G^- peak as TO phonons (i.e. the circumferential in-plane mode) and that the broad asymmetric lineshape is an intrinsic characteristic [10]. In contrast, based on the argument that the available momentum of

incident photons for Raman measurements is too small for energy conservation in phonon-plasmon coupling, coupling to a band of plasmons arising in bundles of SWCNTs has been proposed to be the origin of the Fano lineshape rather than an intrinsic process in single m-CNTs [11]. Comparisons of Raman measurements on individual bundles and single metallic tubes have led to results where the broad, downshifted, and asymmetric G^- peak disappears upon de-bundling by mechanical manipulation [12] or by low density CVD growth [13]. Narrow linewidth and frequency similar to s-CNTs should then be the intrinsic attributes of m-CNTs. However, reference 11 predicts G^- frequency upshift with number of tubes in bundle, in contrast with other references which either show a downshift [14] or tube diameter, not bundle size, dependence of G^- frequency [10, 15] Therefore, the proposed phonon-plasmon/ band of plasmon coupling theory fails to provide an explanation for experimental results.

The discrepancies between reports come from either measurement on bundles of CNTs, where bundling effects and signal overlapping dominates, or the neglect of CNT-environment interactions, for instance, charge transfer and defect formation. We utilize effective polymer electrolyte gating with simultaneous Raman and electrical measurements at individual SWCNT level, as depicted in figure 1.11, to provide new insights, in particular, on how phonon modes involve with changing of the Fermi level.^{16, 17} Such measurements are especially important in elucidating what the inherent phonon lineshape is and therefore what the mechanism that causes the broadening of G^- line is.

2.2. Fano Lineshape and Kohn Anomaly

Figure 2.1 shows D- and G-band regions of the Raman spectrum of a single m-CNT at two different gate voltages, V_g . A single radial breathing mode (RBM) at 202.3 cm^{-1} , which is resonant with 1.96 eV excitation source, indicates that this is a metallic tube. Narrow linewidth, $\text{FWHM} = 6 \text{ cm}^{-1}$, and the consistency of 1.3 nm diameter obtained from AFM imaging with expected diameter of 1.2 nm based on the RBM frequency shows that it is an isolated tube. There are large changes in the G-band upon different V_g . The upper spectrum at $V_g = 1.2 \text{ V}$ in figure 2.1 is fitted with two Lorentzians for the G-band and one Lorentzian for the D-band. Both features of G-band have frequencies similar to typical single s-CNT of comparable diameter [18, 19]. At $V_g = -0.2 \text{ V}$, where the electrical conductance is minimum, which indicates that this potential corresponds to the Fermi level being at the DP between the first pair of vHS, a broad asymmetric Fano lineshape appears. The G-band region of the spectrum at DP is fitted to three Lorentzians and one Fano line. The four features of the G-band are labeled P1 through P4. It is P1 that exhibits asymmetric Fano lineshape near DP but disappears at high V_g . The curve fitting for all data presented here is carried out including the D-band to ensure that changes in the D-band intensity are not mistaken for lineshape asymmetry. In contrast to the high V_g all-Lorentzian spectrum, the asymmetric Fano component arising near DP leads to a non-vanishing intensity well below the D-band region.

In addition to asymmetric lineshape, the spectrum at $V_g = -0.2 \text{ V}$ also exhibits broadened linewidths for all G-band modes. The two dominant peaks of the G-band at $V_g = 1.2 \text{ V}$ exhibit narrow linewidths (FWHM) of $\sim 10 \text{ cm}^{-1}$ whereas the corresponding two peaks (P2 and P3) at $V_g = -0.2 \text{ V}$ have FWHMs $\sim 20 \text{ cm}^{-1}$. The asymmetric component P1 also shows about a factor of 2 increase in linewidth near DP compared to Fermi level

near vHs (FWHM = 62 cm⁻¹ at $V_g = -0.2V$ whereas FWHM = 28 cm⁻¹ and 34 cm⁻¹ at $V_g = 0.4V$ and $-0.8V$, respectively).

The spectral evolution of another single m-CNT with RBM at 203 cm⁻¹ is shown in figure 2.2. In figure 2.2a, gradual narrowing of the broad asymmetric Fano lineshape and frequency upshift are observed from $V_g = 0V$ to 0.9V. The negative V_g region is shown in figure 2.2b. Similar change in the loss of Fano component P1 as in the positive gate voltage region is observed but to a lesser extent. Spectra in figs. 2.2a and 2.2b are fitted in the same manner as the lower spectrum in fig. 2.1. In figure 2.2b, the Raman spectrum prior to polymer electrolyte deposition is also shown. Notice that lineshapes, widths, and frequencies of this tube as-synthesized all resemble spectra at $V_g < -0.5V$. There are two important implications of these observations. First is that the adsorption of polymer electrolyte does not have any noticeable effects other than shifting the Fermi level as expected from reference 20. The second implication is that the Fermi level of the m-CNT in air ambient lies several hundred meV below DP. While debates over whether or not charge transfer occurs from O₂ have mainly focused on s-CNTs [21], m-CNTs with finite density of states around DP should be much more prone to charge transfer. These changes in G-band lineshape imply electron transfer to O₂ which is discussed further in references 22 and 23.

Figures 2.3a and 2.3c compare the V_g dependent frequency shifts of P₁ peak with the electrical conductance. Conductance before (in the dark) and during the Raman measurements are shown together indicating that the low laser intensities used here do not have any significant effect. Considering that polymer electrolyte gating leads to nearly ideal gate efficiencies and that the nanotube is resonant with 1.96 eV incident

laser, the increase in the conductance at positive and negative V_g should correspond to increasing electronic density of states as the Fermi level nears the first pair of vHs. The conductance minimum at $V_g \sim 0.2V$ then corresponds to the Fermi level at DP. The most prominent effect on the Raman spectrum of a single isolated m-CNT as shown in figure 2.3a is the softening of P_1 feature coincident with the conductance minimum. Concurrent line broadening with softening as well as the correlation with conductance of coupling parameter q , shown in figure 2.3b, suggests that electron-phonon coupling becomes stronger near DP for P_1 .

In short, we have shown that Fano lineshape is inherent to single m-CNT and that it is observable when the Fermi level is close to the band crossing point. The Fermi level shift towards vHs changes the Fano lineshape to Lorentzian.

2.3. Physics of Raman Fano Component

Several theoretical studies have assigned the Fano component to the LO mode that is softened by a Kohn anomaly (KA) at the Γ point in the phonon dispersion [24, 25, 26, 27]. The KA, or the sudden softening of phonon frequency resulting from an abrupt change of the electronic screening of atomic vibrations, happens in the LO phonon branch as LO phonon distorts the lattice such that a dynamic bandgap is induced in the electronic structure as demonstrated in figure 2.4 for an armchair CNT [24]. The electronic band structure of CNTs is obtained from band structure of graphene which consists of cones intersecting at 6 corners, K point or DP, of the 2D Brillouin zone, by zone folding argument, i.e. by the intersection of the cones with those planes that are allowed by the conditions imposed by the wrapping procedure [28]. Since the reciprocal lattice can be obtained by turning the real lattice 90° for graphene, the LO mode makes the tip of the

cones moving perpendicular to the allowed lines, hence, opening a bandgap in electronic structure of m-CNT whereas the TO mode only shifts the tip to different k point. The bandgap opening lowers the energy of valence electrons near the DP and the energy gained, few meV, compensates the strain induced by the lattice deformation. However, at ambient temperature, the energy gained by bandgap opening is not sufficient for a static lattice distortion. Instead the corresponding vibrational frequency, or LO frequency, is lowered [24]. In m-CNTs, KA manifests itself as the coupling of LO phonon to vertical transition as indicated in figure 2.5a in which phonon decays to creates an electron-hole pair [27, 29] Clearly, this coupling mechanism is sensitive to position of the Fermi level as the further the Fermi level is shifted away from the DP, the lower the electronic energy is gained by bandgap opening, or the higher the phonon frequency is measured. Moving the Fermi level by electrostatic doping therefore provides a way of tuning the strength of the electron-phonon coupling.

Phonon can be regarded as a perturbation of a crystal. In general, they should be described by time-dependent perturbation theory, given their dynamic nature, Quantitatively, the frequency shift of Fano line is calculated by second-order perturbation theory [27, 29] Taking electron-phonon interaction into account, the phonon energy becomes: $\hbar\omega = \hbar\omega_0 + \Delta\hbar\omega$ in which $\hbar\omega_0$ is the phonon frequency without electron-phonon interaction and the correction term due to the electron-hole pair creation is given

$$\text{by: } \Delta\hbar\omega = \sum_k |W_k|^2 \frac{f(\varepsilon_h(k)) - f(\varepsilon_e(k))}{\varepsilon_h(k) - \varepsilon_e(k) + \hbar\omega + i\delta} \quad (1)$$

Also the electron-phonon contribution to phonon linewidth is given by:

$$\gamma_{LO}^{e-p} = \pi \sum_k |W_k|^2 \delta(\varepsilon_h(k) - \varepsilon_e(k) + \hbar\omega) [f(\varepsilon_h(k)) - f(\varepsilon_e(k))] \quad (2)$$

where W_k is the strength of the electron-phonon interaction in creating electron-hole pair at momentum k , $f(\varepsilon)$ is the Fermi-Dirac distribution with a variable Fermi level E_F , $\varepsilon_e(k)$ and $\varepsilon_h(k)$ are the electron and hole energy, respectively, δ is the decay width, and $\delta(\varepsilon)$ is the Dirac distribution. We need to sum over all possible intermediate electron-hole pair states in equation (1) and (2), which can have energy $\varepsilon = \varepsilon_h(k) - \varepsilon_e(k)$ much larger than phonon energy $\hbar\omega$, and at $T=0$ K:

$$\omega(E_F) = (\omega_0^2 + \frac{2a_0^2\sqrt{3}}{\pi^2 d\beta M} < D_\Gamma^2 >_F \ln \frac{|2E_F + \hbar\omega_0| |2E_F - \hbar\omega_0|}{|2\beta \bar{k}|^2})^{1/2}$$

Electron-phonon contribution to LO linewidth at temperature T :

$$\gamma_{LO}^{e-p}(E_F) = \frac{79cm^{-1}nm}{d} \left[\frac{1}{e^{(E_F - \hbar\omega_0/2)/k_B T} + 1} - \frac{1}{e^{(E_F + \hbar\omega_0/2)/k_B T} + 1} \right]$$

in which a_0 is the lattice parameter, M is the atomic mass of carbon, ω_0 is the bare frequency, the graphene electron-phonon coupling $< D_\Gamma^2 >_F = 45.6 \text{ (eV/\AA}^0)^2$, $\bar{k} = 0.1 \frac{2\pi}{a_0}$,

$$\text{and } \beta = (14.1\text{eV}) \frac{a_0}{2\pi}.$$

At $T=0$ K, the two singularities appear at which the electron-phonon interaction is strongest because the resonance of phonon energy and the real electronic interband excitation. This divergence is responsible for the abrupt change in phonon frequency, or Kohn anomaly. However, we do not see these singularities in our experiment since energy level broadens at higher temperature [25, 27]. Instead, we expect to see LO phonon softening and broadening when Fermi level is close to the DP as demonstrated in figure 2.5b whereas TO frequency should stay constant since TO mode is not supposed to

exhibit KA [25, 27]. Our result on LO phonon qualitatively agrees with this prediction as shown in figure 2.6 and 2.7. The only fitting parameter is the gate coupling efficiency, taken as 0.4. However, the degree of LO phonon spectrum softening and broadening is smaller than the calculated for m-CNT with moderate degree of defect (figure 2.6). For another m-CNT, which does not exhibit significant amount of defect, we see a good fit between theoretical calculation and experimental results (figure 2.7). We also see TO phonon softening and there is no crossing between LO and TO modes as predicted. These discrepancies will be discussed in chapter 3 in light of defect dependence.

In m-CNTs, the strong electron-phonon coupling gives rise to Kohn anomaly in LO mode which is evidenced by LO phonon softening and broadening when the Fermi level is close to the DP. Kohn anomaly softens LO frequency much stronger than curvature effect on TO mode and thus, in m-CNT, the lower frequency peak, G^- , is assigned to LO mode, and the higher one, G^+ , to TO mode [22-25] This assignment is opposite to s-CNTs in which Kohn anomaly is not supposed to occur as their band gap is larger than phonon energy and there is no resonance of phonon energy and interband electronic excitation. This will be discussed further in chapter 4.

The gate dependence of RBM mode is shown in figure 2.7. When the Fermi level is close to the DP, not only the LO mode softens but also RBM mode. However RBM mode softens only 2 cm^{-1} and RBM linewidth stays almost constant over the wide range of gate voltage, in contrast to the broadening of LO phonon mode. The behaviors of RBM mode can be understood by considering that, like LO phonon, RBM phonon can excite vertical electron-hole pairs, thus, renormalizing phonon energy [29, 30]. Nevertheless, RBM phonon energy is 25 meV, a small fraction of LO phonon energy

(190 meV), the electron-hole pair excitations for RBM occur much closer to the DP. At this energy scale the curvature-induced bandgap [31] becomes significant. For this (14,2) m-CNT, the bandgap is 42 meV according to references 30 and 32, which exceeds RBM phonon energy, hence, there is no real vertical transition and linewidth does not broaden.

2.4. References

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2.5. Figures

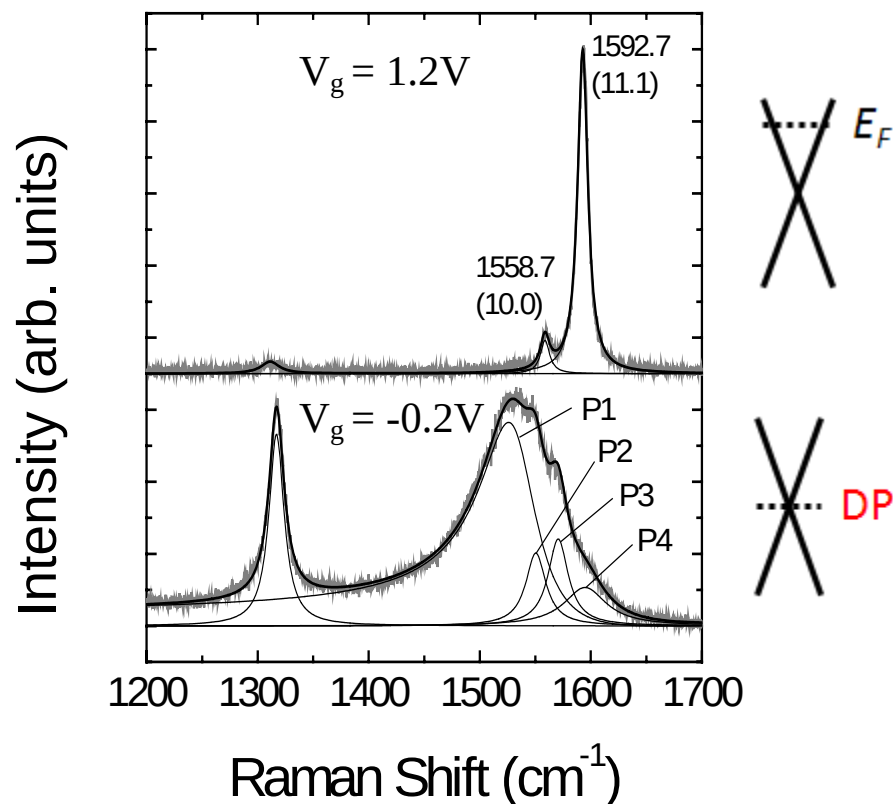


Figure 2.1: Raman spectra of a single isolated m-CNT at the indicated gate voltage V_g (in bold) with corresponding position of Fermi level E_F . Gray lines are the data and the bold black lines are the curve fits as described in the text. Thin lines are components of the curve fit with P1 – P4 designated for lower spectrum. Numbers in the upper spectrum correspond to peak position (width) in cm^{-1} . Spectra are offset for clarity.

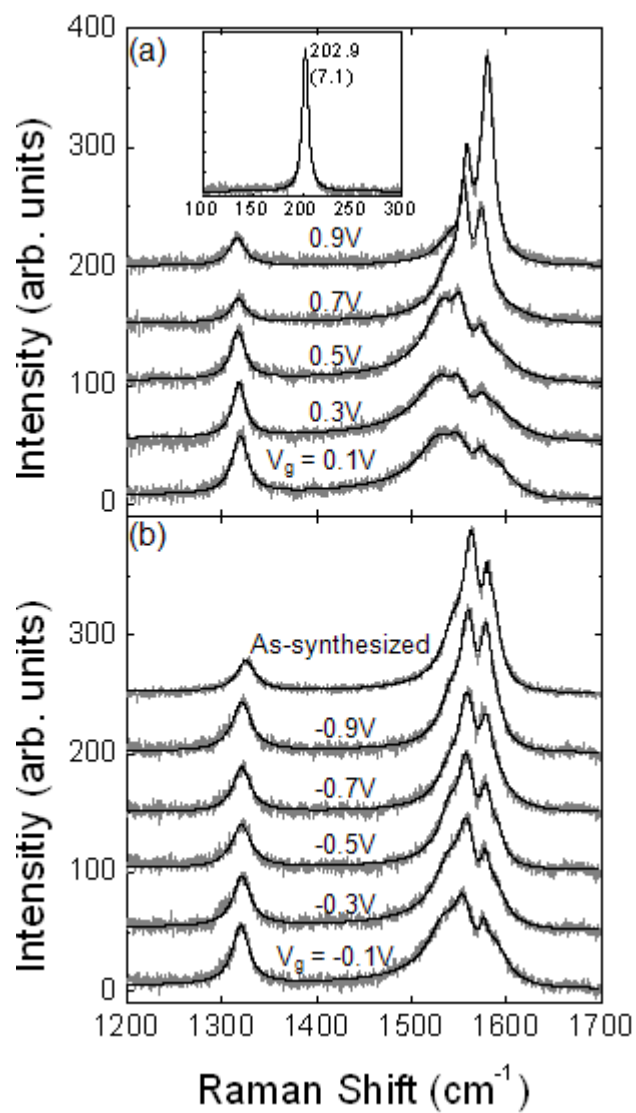


Figure 2.2: Raman spectra of a m-CNT at positive (a) and negative (b) gate voltages V_g swept from -1 to $+1$ V at 0.1 V step. Spectra at 0.2 V intervals and at 0 V are shown and offset for clarity. Top spectrum in (b) and RBM in inset of (a) correspond to the same tube prior to polymer electrolyte deposition without applied V_g . Peak position (width) for RBM is indicated.

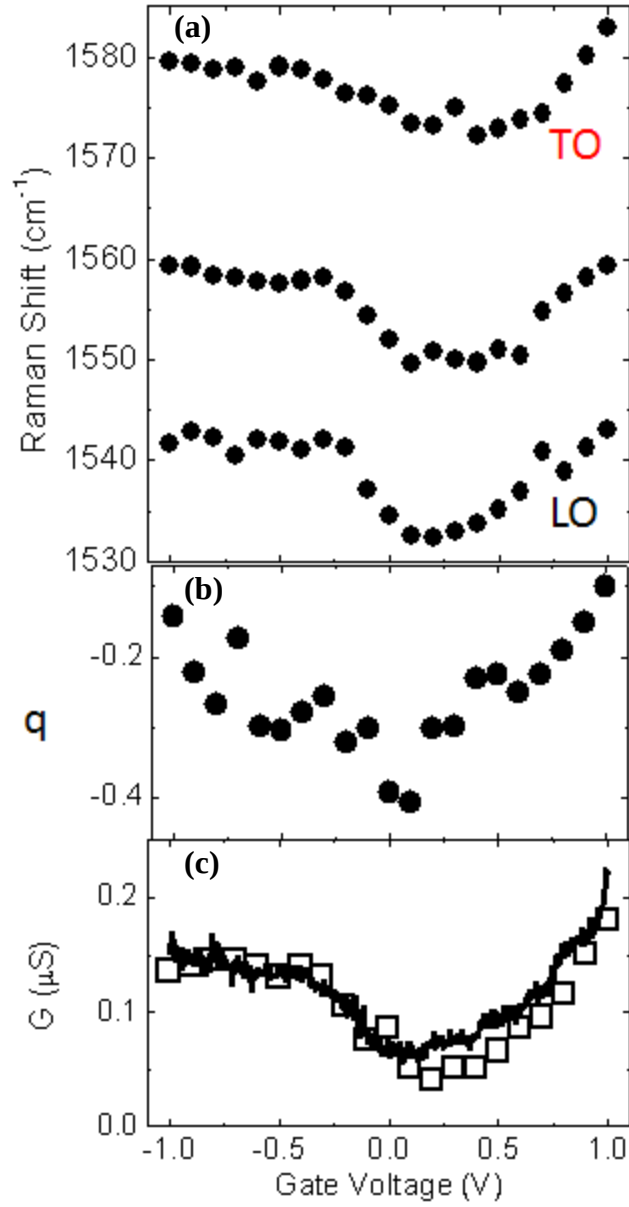
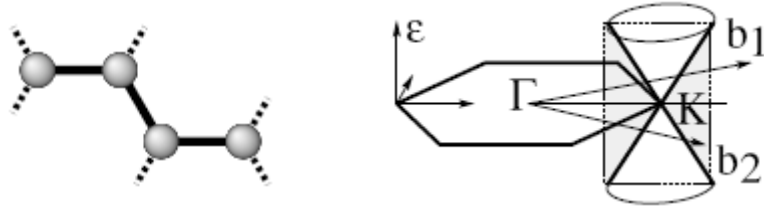
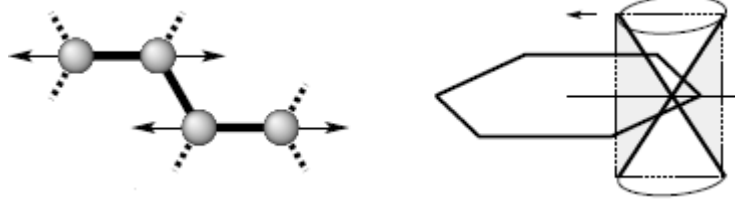


Figure 2.3: V_g dependence of frequency shifts (a) and Fano line coupling parameter q for P1 (b) compared with conductance (c) of the same tube as in figure 2.2. Open squares (line) are conductance during (before) Raman measurements.

a) No displacement



b) TO mode



c) LO mode

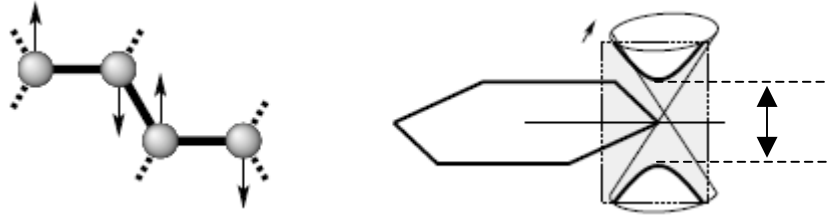


Figure 2.4: (a) Electronic band structure of graphene in the vicinity of K point of the Brillouin zone (hexagon). The thick lines indicate the band structure of an armchair nanotube obtained by intersecting the gray plane with the two cones. (b) For TO mode, the crossing point shifts along the $K\Gamma$ line, thus the band structure of the nanotube does not change. (c) For LO mode, the crossing point shifts perpendicular to the $K\Gamma$ line and opens a gap (double head arrow) [24].

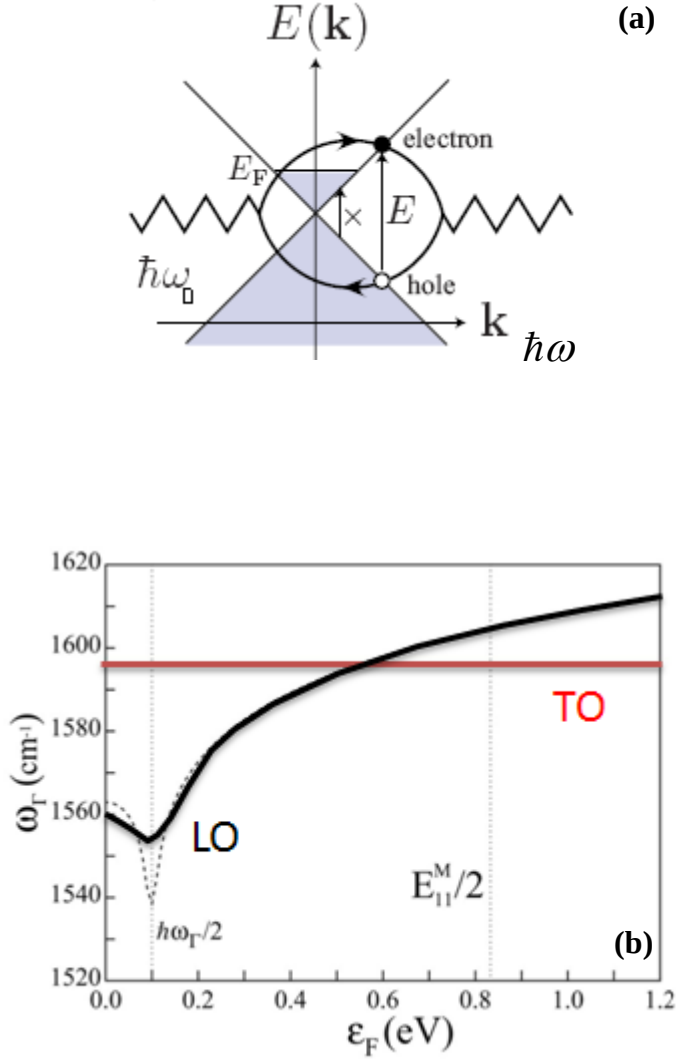


Figure 2.5: (a) An intermediate electron-hole pair (presented by a loop) state that contributes to the energy shift of phonon modes (presented by zigzag lines) is depicted. (b) The predicted dependence of LO and TO phonon frequency on position of the Fermi level for (9, 9) m-CNT [27, 29].

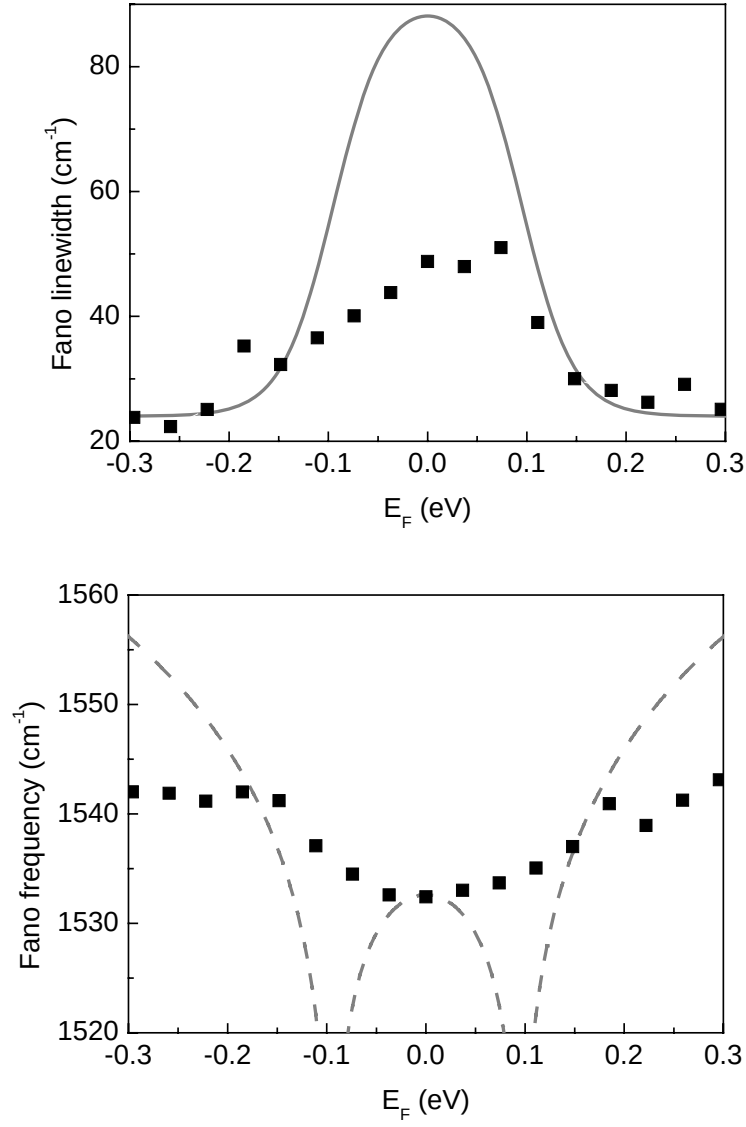


Figure 2.6: Linewidth (upper) and frequency (lower) of Fano component as a function of Fermi level E_F of the same m-CNT shown in figure 2.3. The solid line in the upper panel and the dash line in the lower are the calculated linewidths ($T=300\text{K}$) and frequencies ($T=0\text{K}$) from reference 27. Our experimental results on LO mode qualitatively agrees with theoretical prediction. However, the degree of LO phonon softening and broadening is smaller than the calculated for this m-CNT which exhibits moderate degree of defect.

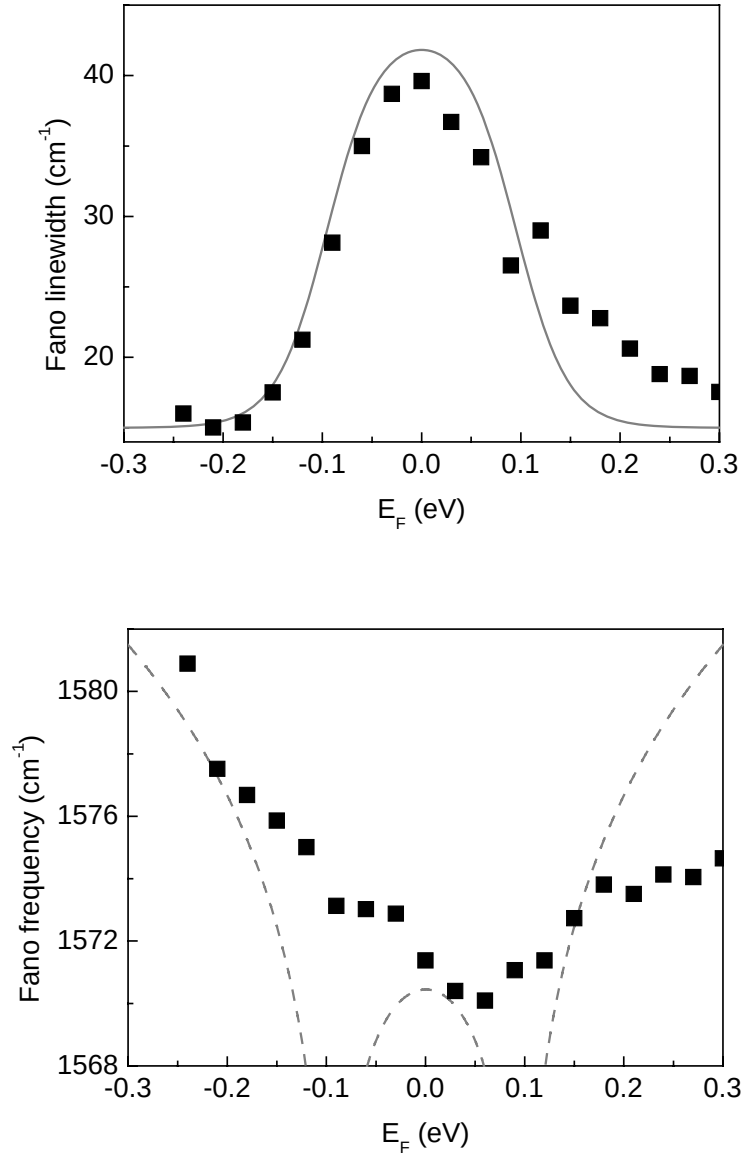


Figure 2.7: Linewidth (upper) and frequency (lower) of Fano component as a function of Fermi level E_F of another m-CNT with RBM frequency at 104 cm^{-1} and nearly free of defect. The solid line in the upper panel and the dash line in the lower are the calculated linewidths ($T=300\text{K}$) and frequencies ($T=0\text{K}$) from reference 27. There is a good fit between experimental data and theoretical calculation.

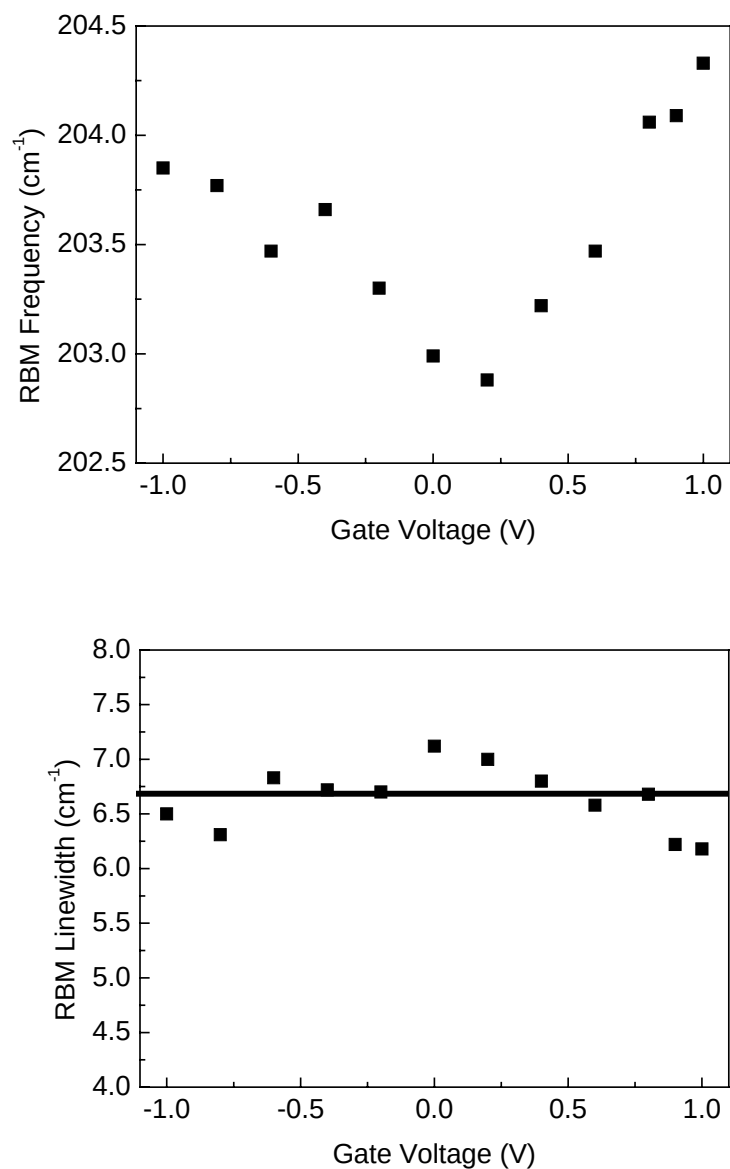


Figure 2.8: Gate dependence of RBM frequency (upper) and linewidth (lower). Straight line guides the eyes. RBM mode softens only 2 cm⁻¹ and its linewidth stays almost constant. RBM phonon can excite vertical electron-hole pairs, thus, renormalizing phonon energy but linewidth does not broaden since there is no real vertical electronic excitation.

CHAPTER 3

DEFECTS IN METALLIC CARBON NANOTUBES

Significant part of this chapter has been published as “Role of Covalent Defects on Phonon Softening in Metallic Carbon Nanotubes”, K. T. Nguyen and M. Shim, *Journal of American Chemical Society* **131**, 7103 (2009). The subsection 3.1 has been published as a part of “Raman Spectral Evolution in Individual Metallic Single-Walled Carbon Nanotubes upon Covalent Bond Formation”, D. Abdula, K. T. Nguyen, and M. Shim, *Journal of Physical Chemistry C* **111**, 17755 (2007), and “Spectral Diversity in Raman G-band Modes of Metallic Carbon Nanotubes within a Single Chirality”, M. Shim, A. Gaur, K. T. Nguyen, D. Abdula, and T. Ozel, *J. Phys. Chem. C* **112**, 13017 (2008).

3.1. Charging, Defect, and Defect Characterization

3.1.1. Doping Dependence of Defect-Induced D-band

In chapter 2, we have discussed about the effect of the Fermi level shift induced by electrostatic doping: the onset of coupling between LO phonon to electronic continuum around DP, or Kohn anomaly. This special coupling leads to the softening of LO mode in Raman G-band when the Fermi level is close to the DP, and the softening is symmetric for electron and hole doping [1, 2, 3, 4]. Another effect is the change of equilibrium lattice parameter that can be seen from charging dependence of Raman D-band phonon energy as shown in figure 3.1 for the same m-CNT that has Raman G-band shown in figure 2.1. When a positive gate voltage is applied, electrons are injected into the antibonding states, resulting in an expansion of C-C bonds [5], and a consequent

decreasing of D-band phonon frequency. In contrast, when holes are injected into bonding states at negative voltages, bond contraction occurs, and D-band frequency increases. In principle, charging dependence of D band phonon frequency is influenced by both electron-phonon interaction [6] and conventional lattice expansion/contraction upon doping. However, impact of the former on D band phonon is one order of magnitude weaker than on G band phonon as reported by several research groups [7, 8]. Therefore, the latter plays dominant role and being partially compensated by the former which results in the doping independence of D band frequency over a range of gate voltage around -0.5V as shown in figure 3.1. The dependence of D-band frequency on doping is different from G-band feature, and can differentiate electron or hole doping.

3.1.2. Degree of Defect Characterization

Although the doping dependence of D band and G band phonon frequencies are different, the ratio of integrated intensities of D and G bands in the Raman spectra has been often used as an indication of covalent functionalization of SWCNTs as well as in identifying amorphous carbon contamination [9]. The rationale for using D to G intensity ratio as a measure of degree of functionalization is from the fact that the D-band arises from disorder scattering. Simultaneous Raman and transport measurement can trace not only G-band but also D-band spectral evolution upon charging, as seen from fig. 2.2a and 2.2b. The enhancement of D-band intensity and the broadening of G-band appear concurrently when the Fermi level is close to the DP. In light of Fermi level shift dependence of G-band lineshapes and D-band intensity, using D- to G-band integrated intensity ratio, I_D/I_G , as an indication of the degree of defect in m-CNTs needs to be considered carefully.

Figure 3.2a shows the gate dependence of I_D/I_G where we have *not* considered the asymmetry of the lowest frequency G-band peak of the same tube. The inset shows the corresponding integrated area under each band for the spectrum collected at $V_g = 0V$. There appears to be a large gate voltage dependence. If I_D/I_G without considering the asymmetry of Fano line is used as an assessment of defect introduction, the increase in I_D/I_G arising from the Fermi level shift can be easily misinterpreted as defect formation as larger degree of defects should lead to a more pronounced D-band. Because the lineshape of the lowest frequency peak of the G-band features converts from Lorentzian to Fano lineshape as the Fermi level shifts from either one of the nearest vHs to the band crossing point, the integrated intensity of the G-band should include the lineshape asymmetry.

Figure 3.2b shows I_D/I_G of the same metallic tube when the Fano lineshape is included as shown in the inset. In this case, I_D/I_G remains independent of the Fermi level shift as it should be since no more physical disorder is introduced. These results indicate that we can utilize I_D/I_G as a qualitative measure of defect formation of metallic tubes *only* if we include the Fano line area which extends below the D-band frequency range, and this is applied in the following section.

3.2. Covalent Defect Introduction to Metallic Nanotubes

3.2.1. Motivation

In light of the fact that most as-synthesized m-CNTs exhibit measurable D-band intensities, an indication of sensitivity of metallic tubes with adsorbed molecules [8, 9, 13], the influence of physical disorder on Raman spectra of m-CNTs needs to be investigated. Figures 3.3a and 3.3b show the LO frequency increasing and LO linewidth

decreasing, respectively, with defect density across several m-CNTs. These behaviors appear to be similar to charging induced changes as discussed in chapter 2, and charging effects and influences of defects need to be sorted out. The relation between the degree of charging and the degree of disorder is also critical especially in characterizing chemical functionalization and doping processes that involve charge transfer. Furthermore, as-synthesized m-CNTs that are exposed to air ambient exhibit a wide distribution of phonon frequencies and linewidths even within a single chirality [10] that makes it difficult to determine the intrinsic parameters, and to compare to theoretical predictions. While much of the distribution has been shown to arise from the variations in the Fermi level position (charging) with one key cause being exposure to ambient oxygen [2, 7, 11], there is no obvious relation between the degree of charging and the degree of disorder, both of which appear upon oxygen exposure. Therefore, interpretation of experimental results remains an issue.

Another complication is in whether or not the Raman TO mode softens as mentioned in chapter 2. There have been apparent discrepancies in experimentally observed behavior of the TO mode – i.e. some reports show TO mode softening [2, 3], some show that it doesn't [1, 5], yet others show both behaviors [12]. While progress has been made in understanding charging dependent Raman spectral changes, very little attention has been given on how disorder complicates these spectral changes. Beyond the increasing D-band intensity and the appearance of the so-called D' shoulder at the high frequency side of the G-band, only limited information about how covalent reactions alter Raman spectra in CNTs is available.

Simultaneous Raman and electrochemical gating studies on single isolated m-CNTs at different stages of covalent defect introduction (i.e. following the same m-CNT while increasing degree of disorder) may separate out the role of disorder from charging effects on the Raman active modes of SWCNTs. Here, we introduce increasing degree of covalent defects via reaction with increasing concentration of 4-bromobenzene diazonium tetrafluoroborate (4-BBDT) and examine the charging dependent G-band Raman spectral evolution of individual m-CNTs after each reaction step with 4-BBDT. Functionalization was carried out with 4-BBDT of desired concentrations in water for 15 minutes. Polymer electrolyte medium, which is described in chapter 1, was removed by rinsing thoroughly with methanol before each reaction and then applied again for subsequent studies. This choice of the chemical reagent for introducing defects may also lead to further insights in developing simple scalable electronically selective chemistry for SWCNTs since 4-BBDT has shown some selectivity towards m-CNTs [13, 14, 15]. Adding covalent chemical groups to the sidewalls influences not only the electronic properties but also the phonon characteristics [16]. Therefore, chemical functionalization may facilitate pathways to electronic and phonon band structure engineering in addition to selectively sorting out metallic and semiconducting SWCNTs for nanoelectronics and sensor applications.

Reaction with 4-BBDT is presumably initiated by charge transfer [10a] and may shift the Fermi level of m-CNTs. Such Fermi level shifts, as we show here, can complicate comparisons between Raman features before and after the reaction because the Raman modes are both charge and defect dependent. By measuring Raman spectra at different electrostatic doping levels, we can directly examine how Raman spectra at the

same Fermi level position, especially near the charge neutrality point, evolve with increasing covalent defects. Changes in charging dependent softening of *both* LO and TO modes of metallic SWCNTs upon covalent defect introduction are investigated. Implications on comparing expected and experimentally observed G-band phonon softening and on Raman characterization of covalent functionalization are discussed.

3.2.2. Influences of Defects on Electrical Properties

In fig. 3.4, we show the D- and the G-band regions of the Raman spectra of a m-CNT at each step of the reaction with 4-BBDT. The inset is the radial breathing mode (RBM) seen at 167 cm^{-1} before the reaction. The Raman spectra are collected with applied electrochemical gate potential to ensure that the Fermi level lies near the DP where the SWCNT is charge neutral. Each spectrum is fitted with one Lorentzian for the D-band around 1320 cm^{-1} and one Fano line and three Lorentzians for the G-band. Following references 2 and 11, we refer to the Fano peak labeled P1 as the LO mode and Lorentzian peak labeled P3 as the TO mode.

Figure 3.5a shows the enhancement of D to G-band integrated intensity ratio, I_D/I_G , of a m-CNT due to increasing reaction concentration of 4-BBDT, at 0, 10 and 50 μM 4-BBDT, confirming introduction of covalent defects. As a consequence of increasing defect scattering, there is a large overall decrease in the conductance from 1.6 μS to $1.4 \times 10^{-2}\text{ }\mu\text{S}$ as seen in figure 3.5a. Figure 3.5b shows how the electrical conductance (normalized to the maximum conductance for comparison), changes upon reaction with 4-BBDT. The enhancement of gate dependence can actually be observed here, i.e. increasing on/off current ratio from ~ 2 before reaction to ~ 300 after reacting with 50 μM 4-BBDT, resulting in semiconductor-like behavior.

3.2.3. Influences of Defects on Phonon Properties

Adding covalent chemical groups to the CNT sidewalls influences not only the electronic properties but also the phonon characteristics. The gate voltage dependence of LO phonon frequency, ω_{LO} , and linewidth, Γ_{LO} , before any reaction and after reaction with 10 and 50 μM 4-BBDT are shown in figures 3.6a and 3.6b. The qualitative dependence to charging is the same in all three cases. That is, the expected phonon softening and broadening of the LO mode occurs near the band crossing point (DP) at all stages of the covalent reaction. The difference lies in the degree of softening and broadening. The decreasing degree of phonon softening and broadening upon increasing covalent disorders is shown for three different m-CNTs in figure 3.7. The main panel is the change in the minimum ω_{LO} ($\Delta\omega_{LO, min}$). The inset is the change in the maximum Γ_{LO} ($\Delta\Gamma_{LO, max}$). Covalent chemical functionalization disrupts the π bonding system by replacing half-filled p_z orbital by an sp^3 bonding orbital at some sites. As a consequence, adding covalent disorders can remove electronic states near the band crossing point and eventually open a band gap in m-CNTs [17]. Increasing defect density from covalent reaction with 4-BBDT then is likely to be reducing the density of states (DOS) near DP which in turn reduces free carrier density. The increasing gate dependence of conductance leading to semiconductor-like behavior after reaction with 50 μM 4-BBDT shown in figure 3.5b supports the idea of reduction in DOS near DP. Carrier scattering from defects would decrease the overall conductivity but does not necessarily lead to enhanced gate dependence. The change in the electronic structure especially about DP then reduces the degree of electron-phonon coupling induced effects (i.e. alleviating the Kohn anomaly induced phonon softening and line broadening) leading to the

observations in figure 3.6 where the degree of LO phonon softening and broadening decreases with increasing covalent defect density.

While the LO mode exhibits behavior consistent with the gradual removal of Kohn anomaly induced phonon softening, increasing defect density leads to *enhanced* softening of the TO mode. Figure 3.8a shows how the gate dependence of ω_{TO} changes with covalent functionalization for the same m-CNT shown in figure 3.4. Data for another m-CNT, which exhibits a larger change, is presented in figure 3.8b. The SWCNT in figure 3.8b initially exhibited no observable D-band intensity and the low degree of initial disorder in this SWCNT may be the main reason for the larger change. Nevertheless, as figure 3.9 indicates, all three m-CNTs examined here show the same trend of TO mode softening near DP with increasing defect density. Another effect of covalent functionalization which introduces local sp^3 defects, disrupting the sp^2 system is the increasing of average bond length, which should then, in principle, lead to softening of all in-plane modes (i.e. both TO and LO modes). This defect induced softening is observed in TO mode which is expected to be independent of Kohn anomaly effects near DP. LO mode, on the other hand, exhibits stiffening with increasing defect density because the reduction in electron-phonon coupling induced effects is dominating the spectral changes.

Besides the softening near the band crossing point, another notable change to TO mode upon covalent functionalization is that it stiffens much more readily upon charging. That is, a much larger change in ω_{TO} can be seen with the same applied gate voltage when the SWCNT is more defective. Because of the electron-phonon coupling matrix element for the TO mode being zero, initial theoretical studies have led to the expectation

that TO mode does not soften like the LO mode and therefore ω_{TO} should be independent of charging [1, 5] However, both charge dependent and independent ω_{TO} have been observed experimentally [2, 3, 9] Most recently, these apparently contradicting results have been suggested to arise from chirality-dependent behavior [9]. Achiral m-CNTs are expected to exhibit only LO mode softening. Chiral m-CNTs can exhibit softening of both LO and TO modes because the TO mode is not exactly along the circumferential direction. While such chirality dependent behavior can be expected, our results in figures. 3.8 and 3.9 indicate that the degree of disorder may sometimes have a larger influence on the observed softening of the TO mode.

In conclusion, we have shown that softening of both LO and TO modes of m-CNTs is sensitive not only to Fermi level position but also to the degree of disorder. With increasing defect density, LO mode stiffens whereas the TO mode softens. These observations imply that reported experimental LO mode frequencies may be higher than the intrinsic frequencies due to the presence of physical disorder, which is observed via measurable D-band intensities in majority of individual m-CNTs. The degree of TO mode softening is also dependent on degree of defects. Covalent disorders complicate the doping dependence of both LO and TO phonon modes and can cause the crossing of LO and TO frequency to be not observable. Furthermore, monitoring chemical reactions that form covalent bonds via Raman spectroscopy should take into account both the Fermi energy position and disorder dependent changes in the Raman features. We have also shown the monotonic dependence of defect induced D-band frequency on the Fermi level position, that is different from Raman G-band and can differentiate electron and hole injection in SWCNTs.

3.3. References

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3.4. Figures

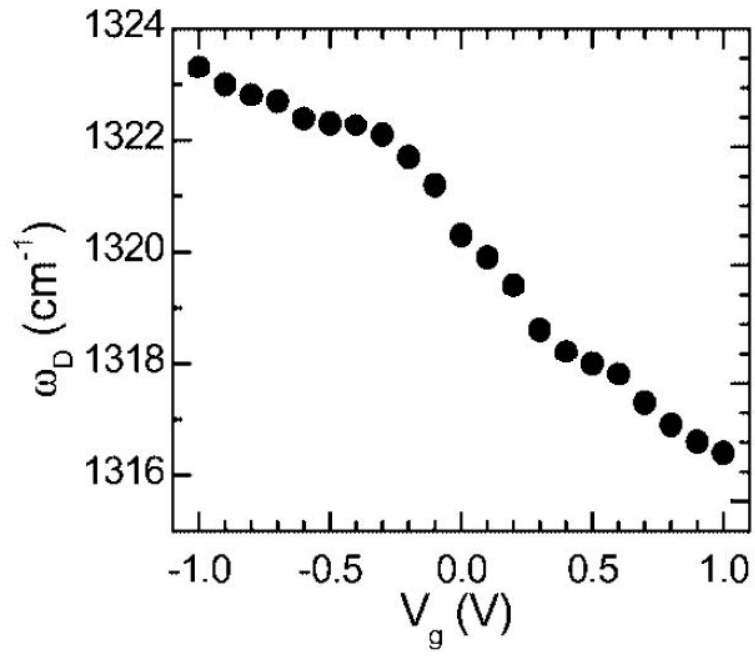


Figure 3.1: Gate voltage dependence of D-band frequency, which can differentiate hole and electron injections.

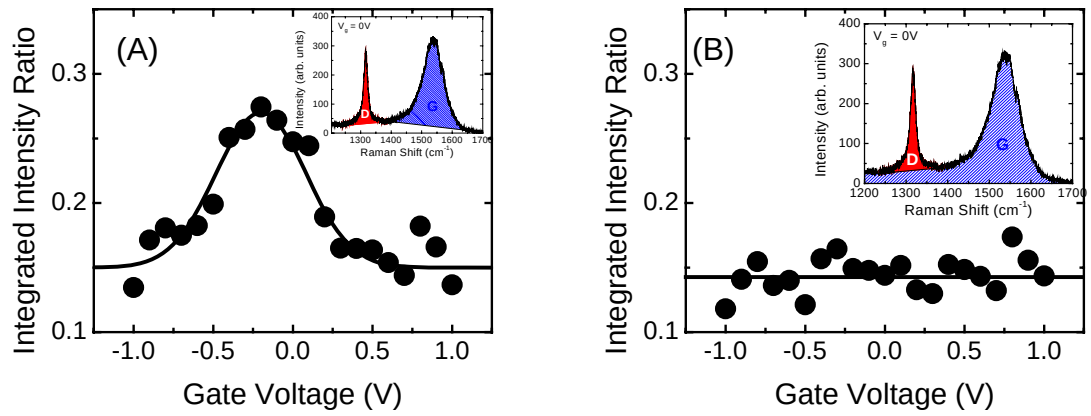


Figure 3.2: Gate voltage dependence of D- to G-band integrated intensity ratios when the Fano lineshape is not considered (A) and when the asymmetric Fano lineshape is taken into account (B). Lines are guides to the eye. Insets show the corresponding integrated areas for the D (red) and G (blue) regions for the Raman spectrum collected at $V_g = 0V$.

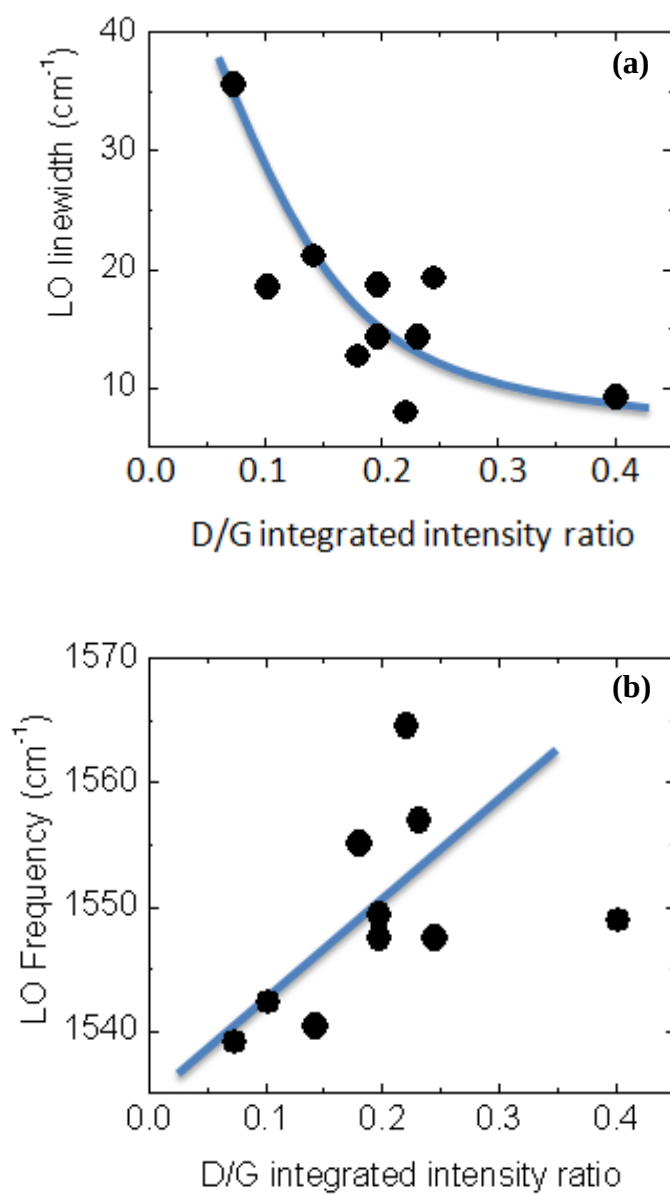


Figure 3.3: Linewidth narrowing (a) and frequency upshift (b) with increasing defect across several m-CNTs, similar to doping induced changes.

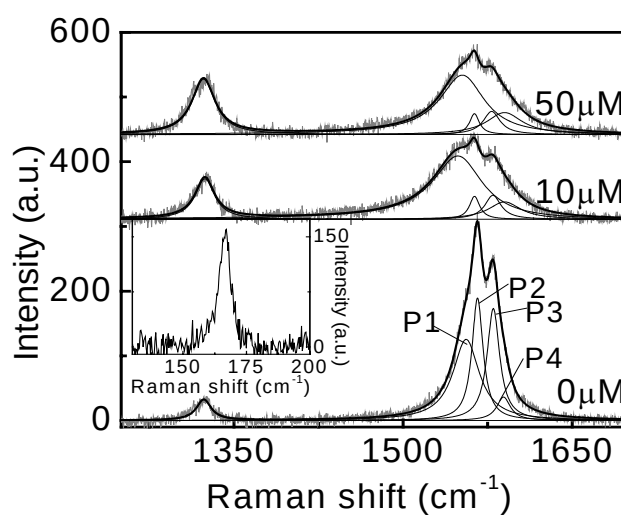
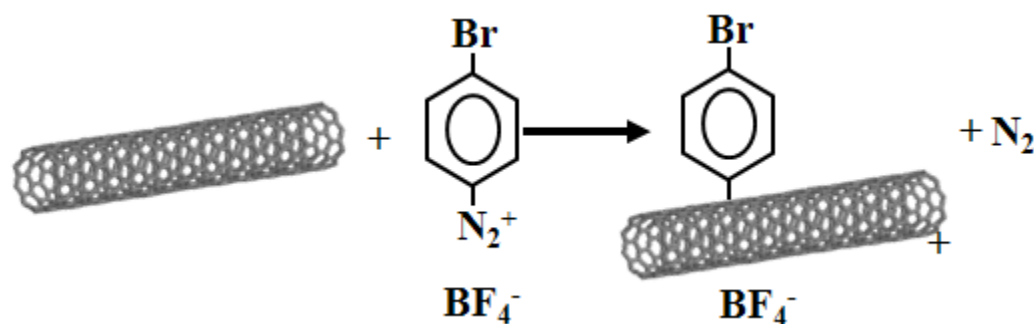


Figure 3.4: *Upper:* Schematic of reaction between m-CNT and 4-BBDT; *lower:* Raman D- and G-band modes along with corresponding curve fits at different stages of covalent defect introduction without polymer electrolyte and without applied V_g . Curve fitting as described in the text is shown along with the spectra. Inset is the radial breathing mode region before reaction.

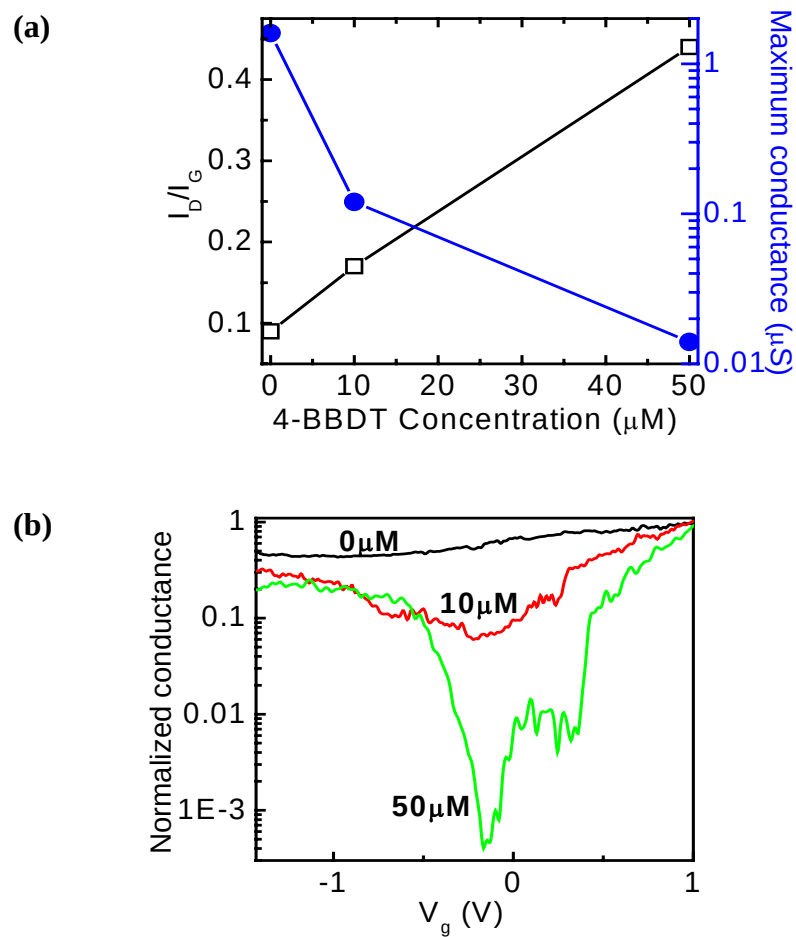


Figure 3.5: Integrated D/G intensity ratio (I_D/I_G) and maximum conductance vs. reaction concentration of 4-BBDT (a). Gate voltage (V_g) dependent electrical conductance of one m-CNT after reaction with indicated concentration of 4-BBDT. The conductance is normalized to the maximum conductance for comparison. “0 μM ” refers to spectrum as fabricated before the reaction (b).

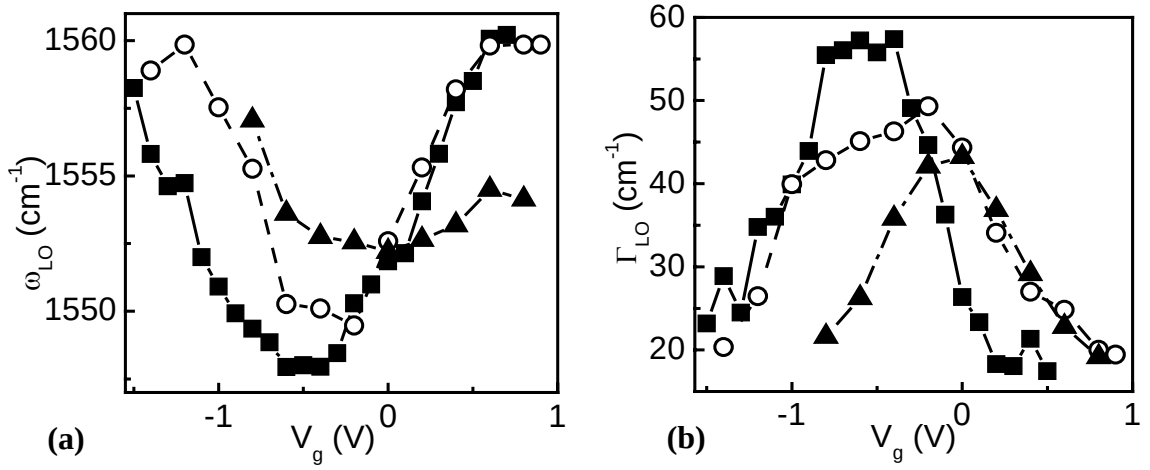


Figure 3.6: Gate dependence of G-band LO frequency (a) and linewidth (b) of the same m-CNT shown in figure 3.4 after reaction with 0 (squares), 10 (circles), and 50 μM (triangles) 4-BBDT concentrations.

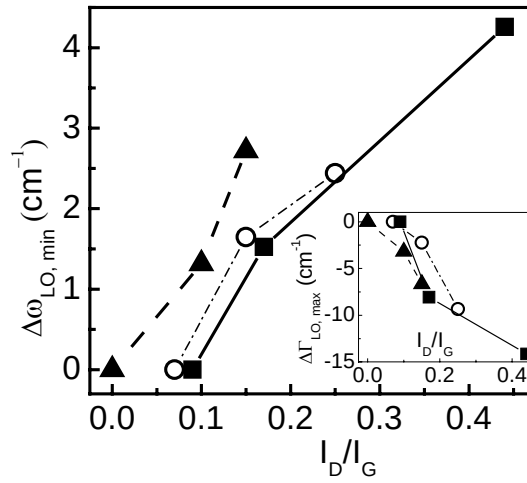


Figure 3.7: Integrated D/G intensity ratio dependence of change in LO mode frequency near the DP for the m-CNT shown in figure 3.4 (squares), for another m-CNT with similar RBM frequency (circles), and for a larger diameter m-CNT with RBM at 105 cm^{-1} (triangles). Inset is the integrated D/G intensity ratio dependence of LO mode linewidth.

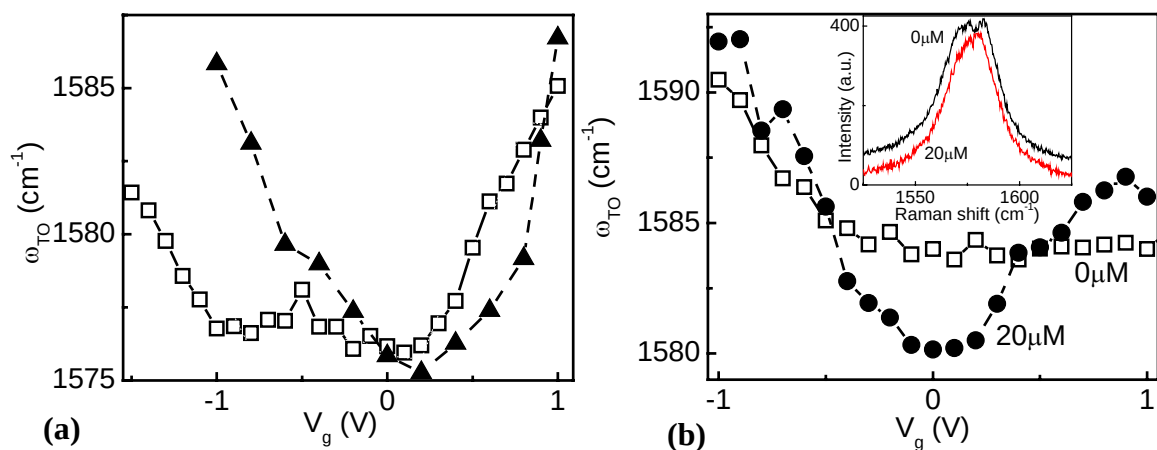


Figure 3.8: Gate dependence of TO frequency after reaction with 0 (squares) and 50 μM (triangles) 4-BBDT concentrations. Data for the same m-CNT as in figures 3.4, 3.5, and 3.6 is shown (a) and another m-CNT with RBM at 105 cm^{-1} is shown in (b). Concentration of 4-BBDT is indicated for this m-CNT. G-band spectra at $V_g = 0$ V (Fermi level near the DP) is shown in the inset. The spectra are offset for clarity.

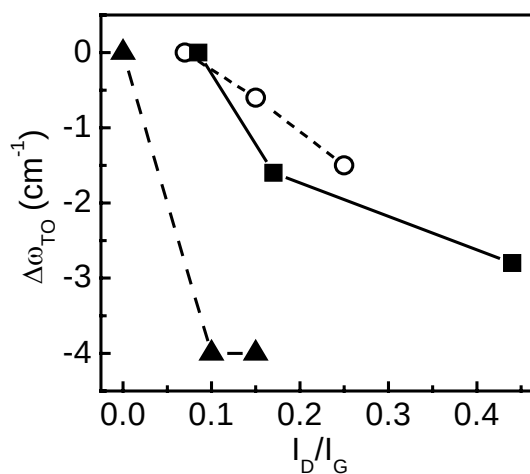


Figure 3.9: Integrated D/G intensity ratio dependence of change in TO mode frequency near the DP for three m-CNTs shown in figure 3.7.

CHAPTER 4

CHARGING AND DEFECTS IN SEMICONDUCTING CARBON NANOTUBES

4.1 Doping Dependence of Raman G-band

Simultaneous Raman and electron transport measurement is becoming a well-established method for investigating isolated m-CNTs under charging and defects [1, 2, 3, 4]. A proper interpretation for the G-band spectra for m-CNTs has been presented in chapter 2, based on the presence of Kohn anomaly which arises from the coupling of phonons to real vertical electronic transitions (i.e, carrier excitation without momentum change) [3, 5]. With the potential application in CNT based transistors, the building block of the next generation electronics, a measure of degree of charging is particular important for s-CNTs. Such a measurement can be done by employing Raman G-band spectra as its frequency can be used as an indication of Fermi level not only in m-CNTs but also in s-CNTs as discussed below.

Group theory predicts six Raman-active features in the G-band region for chiral nanotubes: $2A_1$, $2E_1$, and $2E_2$, which are reduced to three Raman-active bands for the zigzag or armchair tubes [6]. For Raman studies of unaligned s-CNTs, only two main components of the G-band are often considered in the analysis. They are usually referred to as the G^+ and G^- lines, which are found around 1590 cm^{-1} (composed of A_1^{LO} , E_1^{TO} , and E_2^{TO}) and around 1570 cm^{-1} (composed of A_1^{TO} , E_1^{LO} , and E_2^{LO}), respectively [7]. The E_1 and E_2 modes have a much weaker Raman intensity than the totally symmetric A_1 modes [8]. Thus, for semiconducting tubes, the G^+ line is attributed mainly to the diameter-independent A_1^{LO} mode, while the G^- line is assigned to the A_1^{TO} [9].

We have studied the change of G band frequency due to Fermi level shift in s-CNTs by performing combined Raman and electrical measurements. Polymer electrolyte gating was used to shift the Fermi level, which can be quantified by electron transport measurement. Figure 4.1 shows the transconductance of a s-CNT FET device at a source-drain voltage $V_{DS} = 10\text{mV}$. This device turns on at positive gate voltage $V_g = 0.4\text{V}$ (and negative $V_g = -0.8\text{V}$) due to the filling of electrons (or holes) to the first vHs on the conduction (or valence) band of the CNT. For this s-CNT, which shows RBM frequency at 152 cm^{-1} , the laser excitation energy of 1.96 eV matches the third electronic transition, E_{33} , thus, the bandgap is $1.96\text{ eV}/3 = 0.65\text{ eV}$. The gate efficiency may be estimated as $0.65 / (0.4 - (-0.8)) = 0.54$, which is in good agreement with previous report on this type of gating setup.¹⁰ We refer $V_g = -0.2\text{V}$ to the charge neutral stage of that s-CNT as it is half way between threshold voltages.

Figure 4.2 shows the evolution of Raman G-band spectra of the s-CNT at both positive and negative gate voltages. The attenuation of the intensity of G-band when V_g changes from $V_g = 0.4\text{V}$ to $V_g = 1.0\text{V}$ and from $V_g = -0.8\text{V}$ to $V_g = -1.0\text{V}$ is continuous as shown in figure 4.3 and attributed to a weakening of the resonant effect. There is a change in frequency of both LO and TO modes. However, the intensity of TO peak which appears at $\sim 1573\text{ cm}^{-1}$ is quite weak and disappears in the background at high gate voltage. The gate voltage dependence of LO mode is shown in figure 4.4 together with another s-CNT with RBM frequency at 118 cm^{-1} . Both tubes exhibit frequency upshift upon charging but with different magnitudes, which are proportional to nanotube diameter. This diameter dependence of frequency upshift is in good agreement with references 3 and 11. It is 7 cm^{-1} for 2nm diameter CNT, and 4 cm^{-1} for 1.6 nm diameter

CNT. (The diameter d , in nanometer, of CNTs can be approximated by the simple relation $\omega_{\text{RBM}} = 217.8 \text{ nm} \cdot \text{cm}^{-1} / d + 15.7 \text{ cm}^{-1}$) [12].

The charging dependence is surprising since the closely related phenomenon, Kohn anomaly, occurs only in metallic system. The phonon energy increasing is an experimental evidence of the theory of phonon renormalization proposed by Tsang and coworkers³ in which the frequency upshift is caused by the renormalization of the phonon energy induced by the electron-phonon interaction, specifically by the virtual electron-hole pair creation as shown in figure 4.5. The energy renormalization in perturbation theory reduces the phonon energy and has its maximum effect on the neutral charged state of CNT. Upon charging, reducing the phonon renormalization energy leads to upshift of Raman mode. A quantitative description of the energy renormalization is obtained by using equation 3.1 for s-CNTs and the evaluated result for Raman LO shift is:

$$\Delta\hbar\omega_G \approx \lambda \frac{\alpha}{6} \left(\frac{\rho_C}{\rho_0} \right)^3 \left(\frac{d}{d_0} \right)^2 \frac{b^3}{1-b^2}$$

where λ is the electron-phonon coupling constant, the constant α relates the interband electron-phonon coupling strength of LO mode to that of both LO and TO modes and $\alpha \approx 1.1$, ρ_C is induced charge in a carbon atom, the characteristic induced charge on a carbon atom $\rho_0 \approx 0.00085e/\text{carbon}$, $d_0 \approx 2\text{nm}$, $b = \hbar\omega/\Delta$ with Δ is the bandgap [3]. The frequency shift is clearly proportional to the induced charge (i.e, position of the Fermi level), and to the tube diameter d which are both experimentally evidenced in figure 4.4.

The phonon renormalization theory predict the Raman G-band frequency upshift upon charging in s-CNTs but not linewidth, since the bandgap is larger than the phonon

energy, and hence, there is no real electron-hole pairs created. Although the line shift is experimentally evidenced, the charging independence of linewidth is not validated. The gate dependent G-band LO linewidth of the same s-CNTs shown in figure 4.4 is presented in figure 4.6. The linewidth increases up to 4cm^{-1} with increasing gate voltage to 1V. Linewidth broadening upon charging is obvious and has been reported in references 3 and 13. Therefore, there are probably other effects that modulate the gate dependence of LO feature. We suspect that the spatial distribution of charge density due to doping causes the inhomogeneous broadening because LO frequency is sensitive to degree of charging.

4.2. Line Broadening and Blueshift upon Covalent Defect Formation

SWCNTs with sidewall defects can exhibit new properties. For instance, thousand-fold improvement in sensing of hydrogen gas has been achieved with decoration of Pd clusters on SWCNT defect sites in comparison with perfect CNTs [14]. Therefore, it is crucial to study the influences of defects in SWCNTs in order to open a new route toward engineering characteristics of CNT-based electronic devices by creating/controlling defects. Defects can be studied by a number of experimental methods, including Raman spectroscopy. Since phonon spectrum depends on charging in SWCNTs as presented in previous section and in chapter 2, looking at phonon properties is important to learn about charge transfer, the main process in electronic sensors. For m-CNTs, simultaneous Raman and electron transport measurement has been proven to be powerful in studying the role of defect. The same approach is applied here for s-CNTs to understand the role of disorder on phonon properties.

Figure 4.7 shows the differences between Raman features at neutral charged state of pristine tube, a s-CNT with RBM frequency at 121 cm^{-1} , and after reaction with $100\text{ }\mu\text{M}$ BBDT at room temperature for 15 minutes. The appearance of D band at 1325 cm^{-1} after reaction confirms defect creation in the s-CNT. The decreasing intensity of the other two Raman peaks, RBM and G-band, is also another signature of defect formation. This intensity suppression can be understood as a consequence of the weakening of resonance effect caused by disorders.

In contrast to the change of Raman intensity, the RBM peak position at 121 cm^{-1} remains unchanged despite the presence of defects as shown in figure 4.7a. This independence is in good agreement with theoretical prediction¹⁵ and can be explained by the fact that RBM arises from the uniform radial displacement of carbon atoms in the CNT, thus, depends only slightly on atomic structure and on small deviations of CNT surface from the ideal one. Intensity of phonon modes, however, depends on particular atomic structure through electronic structure.

For the Raman G-band, since the G^- peak intensity is weak, we limit our discussion to G^+ mode. As seen from figure 4.7c, G^+ frequency and linewidth increase from 1590 cm^{-1} to 1591.5 cm^{-1} , and from 6 cm^{-1} to 8 cm^{-1} , respectively, upon defect formation. The defect dependence of G^+ feature is clearer in figure 5.8 that shows both charging and defect dependence. The charging dependence of G^+ peak frequency stays almost the same after reaction with 4-BBDT. However, line broadening and slightly frequency upshift upon disorder formation are obvious. The phonon lifetime shortening is a mechanism for linewidth broadening due to defect formation. The primary broadening mechanism in perfect CNT is decay of optical phonon mainly into two acoustic phonons

with opposite wave vectors [16] Nevertheless, in defective CNT, disorders break crystal translation symmetry and the Raman optical phonon can also decay at defect sites due to relaxed momentum conservation requirement. Additional decay path further reduces phonon lifetime, thus, broadening phonon linewidth. Other possible mechanisms responsible for the broadening is defect induced pure dephasing by random elastic scattering and inhomogeneous broadening due to spatial difference of density of defect.

In conclusion, simultaneous Raman and electrical measurement continues to prove to be an effective method in studying charging and defect in s-CNT. Both electron and hole doping result in the LO mode frequency increasing and linewidth broadening. The charging dependences are noticeable when carriers start to be injected into the first vHs and proportional to the tube diameter. For defect effects, besides the appearance of D-band at around 1325 cm^{-1} , defect formation causes Raman intensity reducing and LO phonon linewidth broadening. In contrast, the charging dependence of LO phonon remains nearly unchanged upon defect formation.

4.3. References

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4.4. Figures

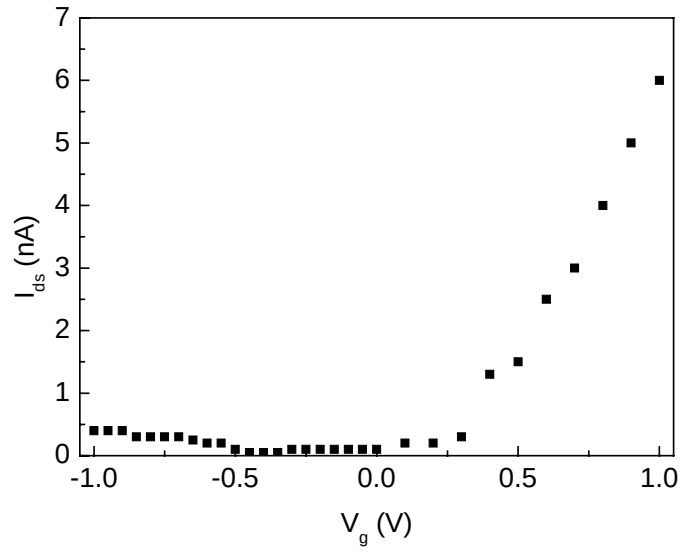


Figure 4.1: Gate dependence of s-CNT with RBM at 152 cm^{-1} . This device turns on at $V_g = 0.4 \text{ V}$ and $V_g = -0.8 \text{ V}$ due to the filling of carriers to the first vHs of the s-CNT.

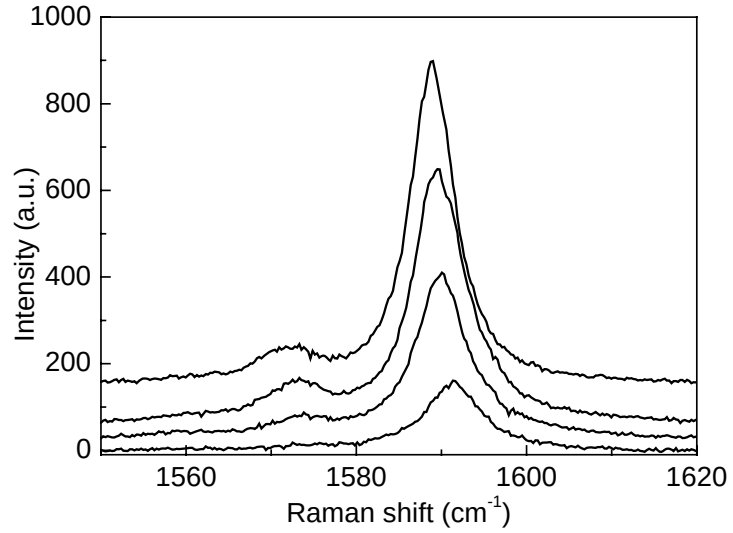
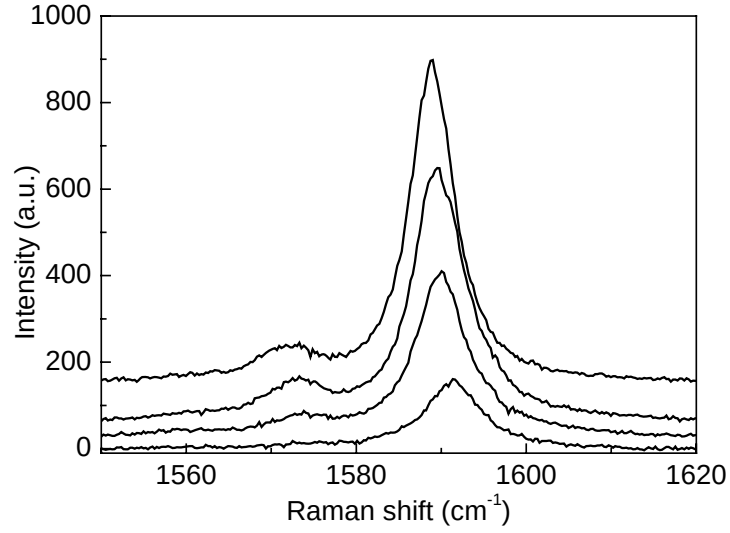


Figure 4.2: Evolution of Raman G-band spectra of the s-CNT with RBM at 152 cm^{-1} at (a) positive gate voltages V_g (from top to bottom: $V_g = 0.2\text{V}$, 0.5V , 0.8V , and 1.0V) and (b) negative gate voltages V_g (from top to bottom: $V_g = -0.1\text{V}$, -0.4V , -0.7V , and -1.0V).

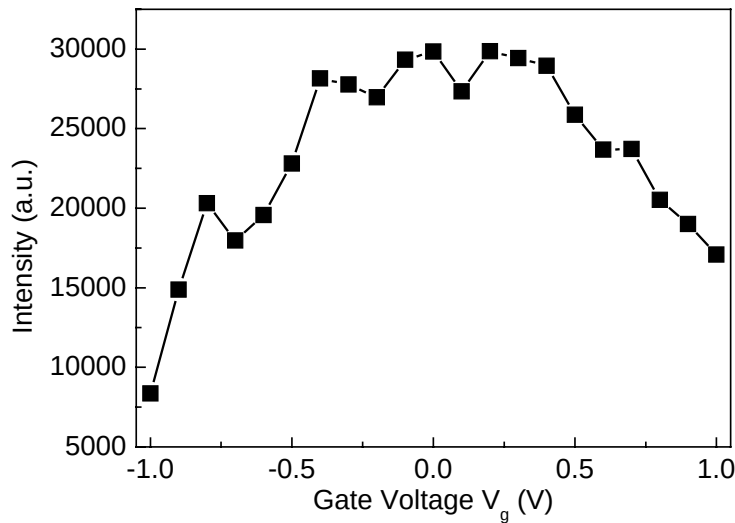


Figure 4.3: The weakening of Raman G-band intensity of the same tube shown in figure 4.2 upon doping.

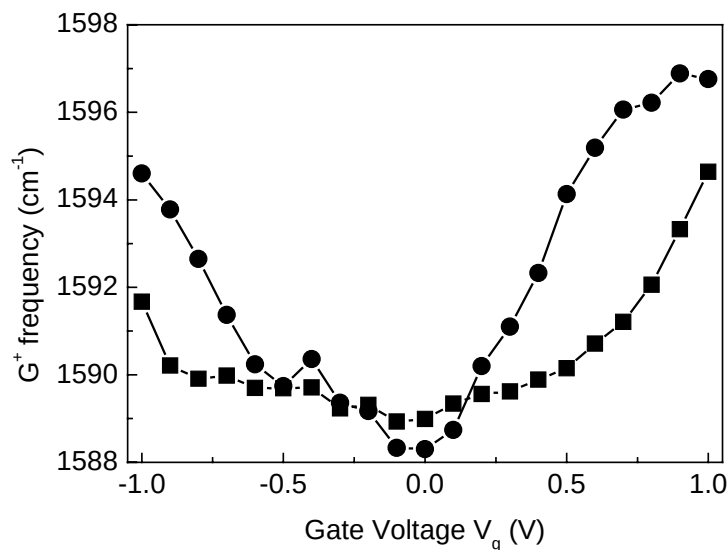


Figure 4.4: Gate dependence of G^+ frequency in different s-CNTs with RBM frequency at 152 cm^{-1} (black squares) and 118 cm^{-1} (black dots). Both tubes exhibit frequency upshift upon charging but with different magnitudes, which are proportional to nanotube diameter.

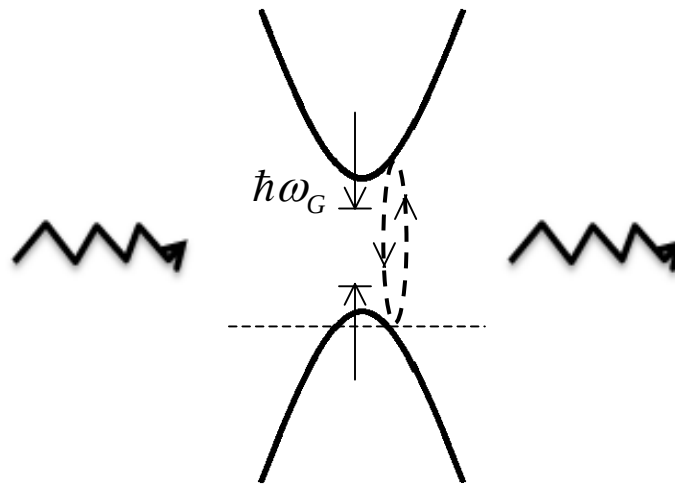


Figure 4.5: Phonon renormalization of the Raman G-phonon by excitation of virtual electron-hole pairs in s-CNTs. Since phonon energy is smaller than the bandgap, no real carrier excitation is possible [3].

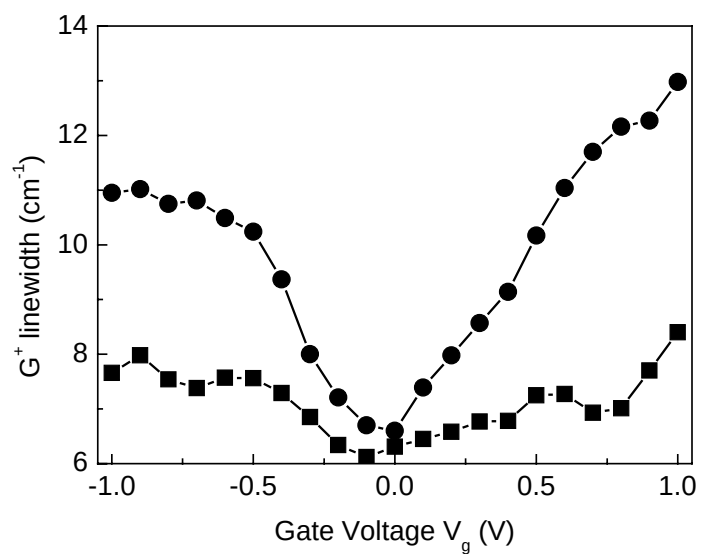


Figure 4.6: Gate dependence of G^+ linewidth in the same s-CNTs shown in figure 4.4 with RBM frequency at 152 cm^{-1} (black squares) and 118 cm^{-1} (black dots). Linewidth broadening upon charging is obvious.

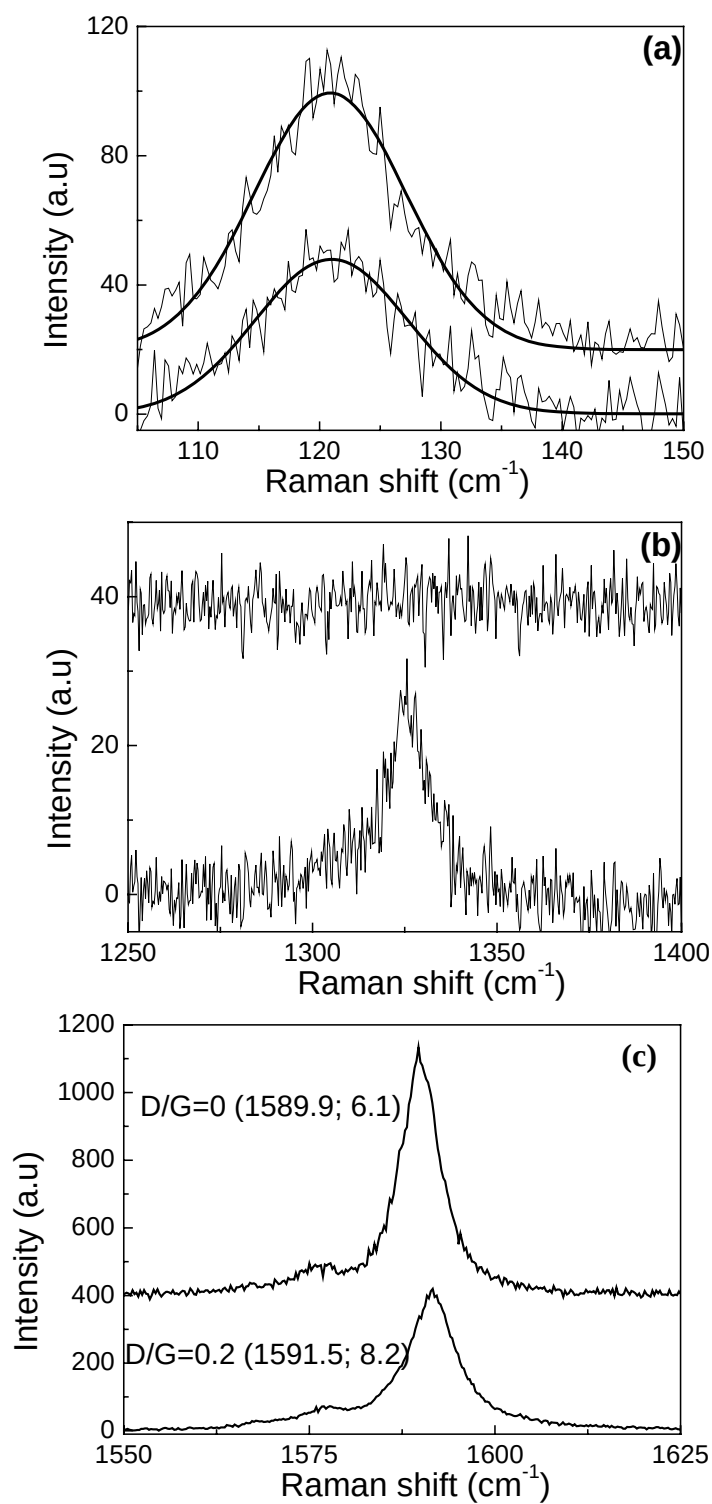


Figure 4.7: Raman spectra of pristine tube (top) and defective tube (bottom): RBM (a), D-band (b), and G-band (c).

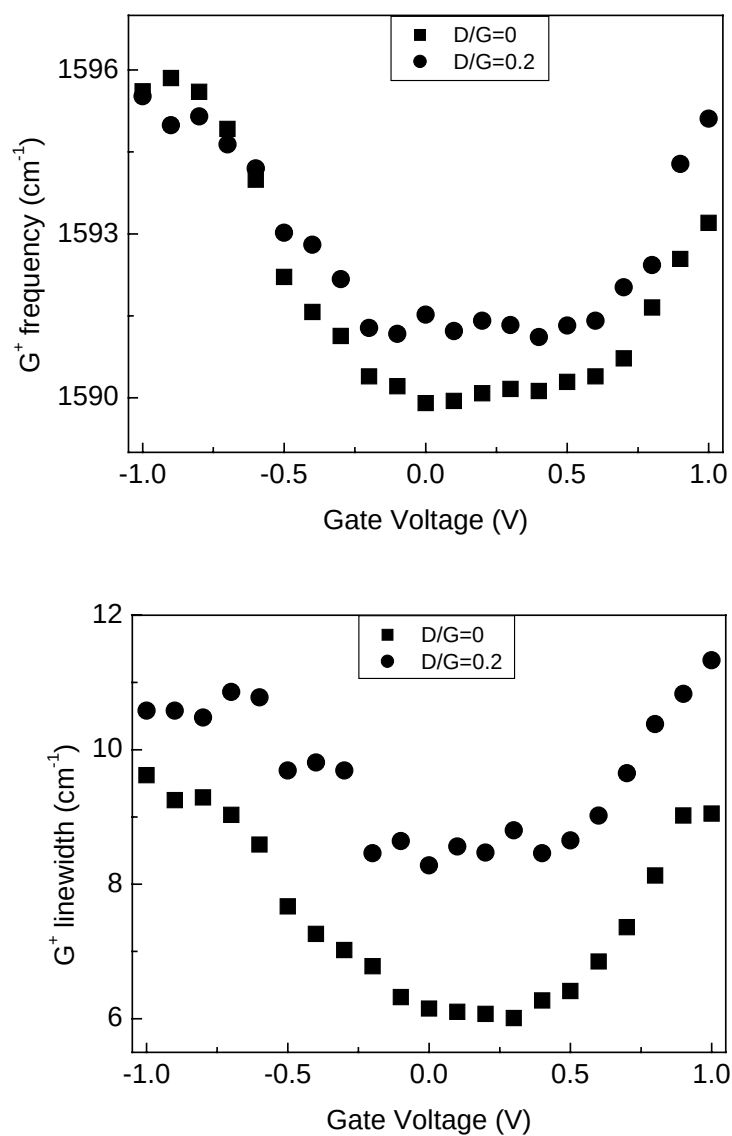


Figure 4.8: Gate dependence of G^+ peak frequency (upper) and linewidth (lower) of pristine tube (black squares) and defective tube (black dots). The charging dependence of G^+ peak frequency stays almost the same after reaction with 4-BBDT. However, its linewidth increases due to disorder formation.

CHAPTER 5

DOPING GRAPHENE

Due to its structural simplicity (two atoms per unit cell) and being a prototypical two-dimensional system, graphene, building block of CNT, has been intensively investigated in theory in the last 60 years [1] However, only recently has it been possible to produce a real single atomic layer of carbon atoms [2, 3] The discovery of Novoselov et al. in 2004 of a simple method (using scotch tape) to transfer a graphene layer from the c-face of graphite to a substrate suitable for measurements of its electrical and optical characteristics has renewed interest in its physical properties and potential applications. Possessing extremely high carrier mobility [4, 5] resulting from linear electronic band dispersion [6], graphene has been extensively studied for future electronics [2, 7, 8, 9, 10]. Interest in potential applications of graphene is more pronounced due to the possibility of wafer-scale graphene synthesis [11, 12]. This would allow the fabrication of individual devices and wiring within “graphene wafer” in the same way that a silicon wafer is processed in current silicon industry. Nevertheless, in graphene, valence band and conduction band touch at Dirac points (six corners of a 2D Brillouin zone, as shown in figure 5.1). Such structures cannot be switched off at room temperature for practical purposes and application of a gate voltage produces only small changes in the device current-voltage characteristic [2, 13] Therefore, it is necessary to develop a bandgap in graphene for potential electronic applications and this is discussed in section 5.1. We also discuss temperature and charging characterization of graphene in section 5.2 since charge transfer and thermal effects play a crucial role in graphene-based devices.

5.1. Chemical Doping with 4-Bromobenzenediazonium Tetrafluoroborate

Graphene bandgap engineering has focused on the utilization of lithographic methods to cut graphene into nanoribbons which physically confine carriers and create an electronic gap [14, 15, 16]. However, edge effects also play crucial role in determining bandgap opening in nanoribbons [17]. The physical deformation at graphene edge caused by edge terminations (e.g., hydrogen passivation) is responsible for the presence of a bandgap besides edge type and graphene width, and complicates the situation. Another bandgap engineering method is application of chemistry. Covalent reactions can be used to change the hybridization of carbon atoms from sp^2 to sp^3 , and inducing a gap. Such chemistry has been shown to be effective in modifying electronic properties of m-CNTs in chapter 3 as these sidewall reactions serve to introduce a bandgap [18, 19]. In this section, we will discuss how the same covalent chemistry affects electrical and Raman characteristics of in graphene.

Graphene samples were prepared via mechanical exfoliation of highly oriented pyrolytic graphite on SiO_2/Si substrate with 300nm thick oxide layer. Graphene flakes were identified by their color, almost transparent, under 100X microscope and by their Raman 2D bands. Electrodes of graphene-based FETs were fabricated by conventional photolithography as described in chapter 1 for CNTs. The same method of functionalizing CNTs with 4-BBDT does not cause defects in graphene at room temperature, as D-band did not show up in Raman spectra both before and after functionalization. Therefore, reactions at different temperatures, 50°C and 75°C, were carried out to introduce different degrees of defect in graphene.

Figure 5.2 compares Raman spectra collected with 633 nm excitation source of a graphene sheet before and after BBDT exposure at 50°C and 75°C. A single, sharp Lorentzian lineshape of 2D peak (32 cm^{-1} linewidth) at 2647 cm^{-1} before reaction is an indication of single-layer graphene [20, 21]. It is noted that turbostratic graphite (i.e., without AB stacking) also exhibits single 2D peak [22]. However, its linewidth (50 cm^{-1}) is much broader than that of 2D peak of graphene. The absence of defect-induced D-band confirms the high quality of the graphene sheet after the device fabrication process. After the reaction, the appearance of D-band and the increasing of D- to G-band integrated intensity ratio evidence defect formation. Raman mapping (figure 5.3), which measures Raman spectra at different positions of the graphene flake, shows D peak at every spots after chemical modification at 75°C, confirming introduction of disorders.

While large changes in the Raman spectra can be observed at different stages of functionalization, the transfer characteristics, on the other hand, indicate that 4-BBDT exposure does not significantly alter the current at the neutrality point (the minimum current) or drastically change the gate dependence of the device as shown in figure 5.4. There is only a positive shift of DP after the reaction, indicating p-type doping from 4-BBDT as expected [21]. The lack of on/off ratio enhancement suggest a low coverage of covalent bonds since significant covalent functionalization should lead to carrier scattering and band structure modification. This is in contrast to the large D/G ratio which should correspond to an effective crystallite size of $\sim 20\text{ nm}$, comparable or smaller than room temperature electron mean free path (few hundred nm). A possible explanation may be that the large fraction of diazonium cations decomposes into other chemicals which only physically adsorb on the graphene surface [23].

Exposure to 4-BBDT does not increase on/off ratio in graphene-based device which is in contrast to gate-dependence enhancement due to covalent defects in m-CNTs as described in chapter 3. This may be because the strained configuration induced by curvature of CNTs facilitates covalent reaction with 4-BBDT [24]. Different functional groups or different conditions for the reaction may work for graphene.

5.2. Doping and Temperature Dependence

Raman G band has been shown to be an effective tool to probe both degree of charging and temperature of graphene. The G band is very sensitive to doping due to strong coupling of phonon to vertical excitation (i.e, carrier excitation without momentum change) because of the presence of Kohn anomaly [25, 26], and this interaction is strongly dependent on the Fermi level position [27]. It has been shown that the G band frequency can be used to effectively monitor charge transfer in graphene device as doping graphene leads to hardening and narrowing of G band phonon spectrum [25]. In addition, similar to CNTs, graphene exhibits significant sensitivity to its surrounding, especially charge transfer from absorbed molecules in its electrical characteristics [24]. Recent transport measurements have indicated that graphene transistors show p-type doping in ambient air. In fact, most measurements require an application of external gate potential to shift Fermi level in graphene to the DP (i.e., its charge neutrality point) [27]. Oxygen adsorption has been shown to induce the p-type doping [28, 29]. Therefore, G band frequency is sensitive to ambient surrounding of graphene.

G band phonon energy also depends on temperature and Raman spectroscopy can be used as a metrology tool for graphene-based devices [30]. When the temperature

increases, the Raman G band frequency decreases as a result of phonon-phonon interactions [31] and G peak position, in turn, can be employed to estimate graphene temperature. However, complication arises from the fact that G mode frequency depends not only on temperature but also on charge transfer resulting from molecular adsorption from the ambient. This necessitates the differentiation of response of G band to doping and temperature in order to use Raman spectroscopy as an effective tool to monitor temperature in graphene. Controllably introducing charge to graphene at each temperature rise under Ar atmosphere can help to separate these effects as discussed below.

Graphene-based FET fabrication has been described in previous section. The FET is then mounted on a ceramic chip carrier which is placed in an airtight heating stage having an inlet and an exhaust for gas flow. Raman spectra were acquired by using a 100x long working distance air objective. Again, a single, sharp Lorentzian 2D feature (30 cm^{-1} linewidth) at 2644 cm^{-1} confirms that all measurements were performed on single layer graphene. All Ar annealing was carried out with a flow rate of $20\text{ cm}^3/\text{min}$ and heating and cooling rate of 20 K/min . Spectra were collected 20 min after each temperature of interest was reached (298 K, 387 K, 471 K, and 560 K) and desired gate voltage was applied. Raman G band and 2D band spectra with Fermi level position at the DP and at different temperatures are presented in figure 5.5.

Figure 5.6 shows gate dependence of G band frequency at different temperatures during the first heating process in Ar. The softening of G band phonon when the Fermi level is near the DP due to the presence of Kohn anomaly occurs at all four temperatures. However, the gate voltage corresponding to the DP (at $V_g = 20\text{V}$) is different at room

temperature compared to the other three temperatures. Even with a mild Ar annealing temperature of 387K, DP shifts to $V_g = 0V$. Figure 5.7 shows a negative shift in transfer characteristics of the graphene-based FET measured simultaneously with the Raman data of figure 5.6. The charge neutrality point shifts from $V_g = 20V$ at 298K to $V_g = 0V$ from 387K. The observed changes are indicative of reduction of p-type doping by thermal removal of oxygen from the sample. The increasing source-drain current with temperature is likely due to better contacts and removal of adsorbed molecules upon Ar annealing. We note that the direct experimental evidence for oxygen effects in graphene and metallic CNTs, a closely related material, has been presented in references 30 and 32. Figure 5.8 shows that heating up to 560K and cooling back to room temperature under Ar leads to improved device performance. The minimum current increases from $0.84 \mu A$ to $2 \mu A$ and carrier mobility is enhanced significantly. When p-doping effects of oxygen is removed, more intrinsic behaviors of graphene is shown in figure 5.9 where the repetition of gate dependent G mode frequency shift during subsequent cooling and heating processes and the correspondence between zero gate voltage and the DP at all temperatures are obvious. The gate dependence during the first and second heating is also plotted together in figure 5.6 for comparison. There is not only the negative shift of charge neutrality point at room temperature as mentioned but also decreasing G band frequency at the same temperature during the second heating compared to the first one. This suggests that the influence of graphene-substrate interaction might change after the first heating as heat treatment can modify chemical structure of the substrate surface to a more stable form.

In addition to the softening due to the presence of Kohn anomaly, or electron-phonon interaction, G band phonon frequency softens upon temperature rise due to phonon-phonon interaction³¹ as seen from figures 5.6 and 5.9. The temperature dependence of G peak position is not in agreement between the first and second heating as majority of ambient effect (e.g. removal of adsorbed molecules from the ambient) is removed during the first heating step. The temperature dependence determined from spectra corresponding to $V_g = 0V$ is presented in figure 5.10 for both the first, second, and third heating steps where the Fermi level is at DP in the second and third ones. First heating step from 298K to 560K leads to G mode redshift of 9.5 cm^{-1} whereas second heating step of the same temperature range leads to a redshift of 7.5 cm^{-1} . The G band frequency shift can be described by the relation: $\omega = \omega_0 + \alpha T$ where α is the first order temperature coefficient. The extracted value from figure 5.9 is $\alpha = -0.035 \text{ cm}^{-1}/K$ and $\alpha = -0.030 \text{ cm}^{-1}/K$ for the first and second heating steps, respectively. There is a 15% difference between the two. Doping from adsorbed molecules shifts the Fermi level in graphene, resulting in the change of G peak position, thus Fermi level need to be ensured at the same position before making any conclusion.

Figure 5.10 shows the temperature coefficient α extracted from figure 5.9 at different gate voltages. The temperature coefficient stays almost the same, around $-0.030 \text{ cm}^{-1}/K$, over a wide range of gate voltage. The electron-phonon interaction plays a minor role in temperature dependent line shift, thus phonon-phonon interaction is the dominant factor, which is in good agreement with theoretical calculation [31]. For a given temperature, the softening of the Raman G band phonon arises from an anomalous screening of the atomic displacements due to electrons close to the DP. The occupation of

these electronic states depends on temperature through Fermi-Dirac distribution. Therefore, in principle, changes in temperature may result in a modification of the electronic screening, which can renormalize the G mode energy. However, as we can see from figure 5.11, this contribution is negligible in comparison to phonon-phonon interaction, specifically, 4-phonon scattering process in which G band optical phonon decays into 3 lower-energy phonons according to reference 31. Based on the charging independence of G band frequency shift, temperature coefficient of graphene is then determined over a wider range of temperature compared to what has been shown in figure 5.10. Temperature dependence of G mode frequency from 598K down to 173K, after annealing sample at 598K in Ar ambient for 1hour in order to remove oxygen and keep the Fermi level at the DP, is presented in figure 5.12. Temperature dependence of G band frequency is well fitted by function $\omega = -0.03T + 1597.5$. The same value of temperature coefficient α , $-0.03 \text{ cm}^{-1}/\text{K}$, confirms the previous result from figure 5.11.

In contrast to G band frequency, contribution to G band linewidth from electron-phonon coupling depends strongly on temperature [29, 31]. Figure 5.13a shows the dependence of G band linewidth on gate voltage at different temperatures. The linewidth broadening at the DP is obvious at all temperatures but the degree of broadening decreases with temperature increase, also the gate dependence profile broadens. When the Fermi level is close to the DP, the linewidth exhibits an unusual decrease with temperature rise. It decreases by 5 cm^{-1} from room temperature to 560K as shown in figure 5.13b which shows a good fit with DFT calculation [31]. Electron-phonon and phonon-phonon interactions contribute to G mode linewidth in opposite ways. While the latter causes the usual linewidth broadening upon heating due to decay of an optical

phonon into acoustic phonons, the former decreases linewidth because of thermal-induced doping [29, 31]. Figure 5.13a clearly shows that, close to the DP, electron-phonon coupling is the dominant factor and is only partial compensated by phonon-phonon interaction. When the Fermi level moves away from the DP, the electron-phonon coupling is weakened and phonon-phonon interaction becomes more important. This is evidenced in figures 5.13a and 5.13c where G band linewidth increases slightly upon heating at high gate voltages.

Finally, we consider temperature dependence of Raman 2D mode at different gate voltages. Figure 5.14a and 5.14b shows similar gate dependence behavior of 2D peak position to G peak but with half of the magnitude of frequency upshift upon doping. The temperature coefficient of 2D mode is $-0.05 \text{ cm}^{-1}/\text{K}$ and also nearly independent of gate voltage as seen in figure 5.14c. In contrast to frequency, 2D band linewidth does not exhibit significant change due to charging (figure 5.15a). This gate independence behavior suggests that the impact of electron-phonon coupling on 2D band linewidth is negligible compared to that on G mode linewidth [22]. Figure 5.15b shows broadening of 2D band linewidth upon heating as expected from phonon-phonon interaction. However, it broadens only 2 cm^{-1} from room temperature to 560K.

5.3. Conclusion

We have shown our work on doping single layer graphene by chemical, 4-bromobenzenediazonium tetrafluoroborate, and by gate potential by utilizing simultaneous Raman and electrical measurements. For chemical doping, 4-BBDT has been shown to p-dope and create defects in graphene. However, the coverage of covalent bond formation is low, therefore, reaction with 4-BBDT does not help to open an

electronic bandgap in graphene as in metallic SWCNTs as discussed in chapter 3. We also mentioned the importance of utilizing not only Raman spectroscopy but also electron transport measurement to investigate defects in graphene as together they provide more comprehensive information. By electrostatic doping, we have shown that ambient air can shift the Fermi level in graphene, hence, shifting the Raman G peak position and modifying the temperature coefficient of G band frequency. The same Fermi level position needs to be ensured in studying how G mode shifts with temperature. The temperature coefficient thus determined is $-0.030 \text{ cm}^{-1}/\text{K}$ at all gate voltages. This gate independence tells us that phonon-phonon interaction play dominant role, not electron-phonon interaction, in temperature dependent line shift.

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5.5. Figures

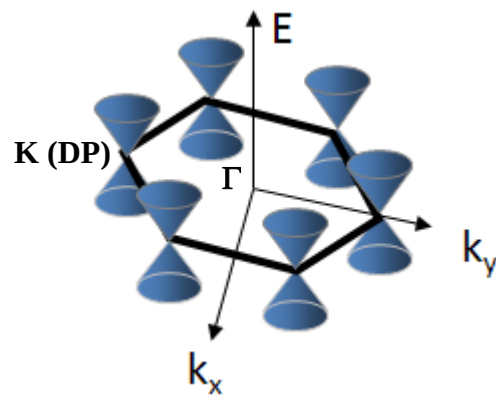


Figure 5.1: Electronic dispersion for graphene near the 6 corners of 2D Brillouin zone. Valence band and conduction band touch at DP (or K point).

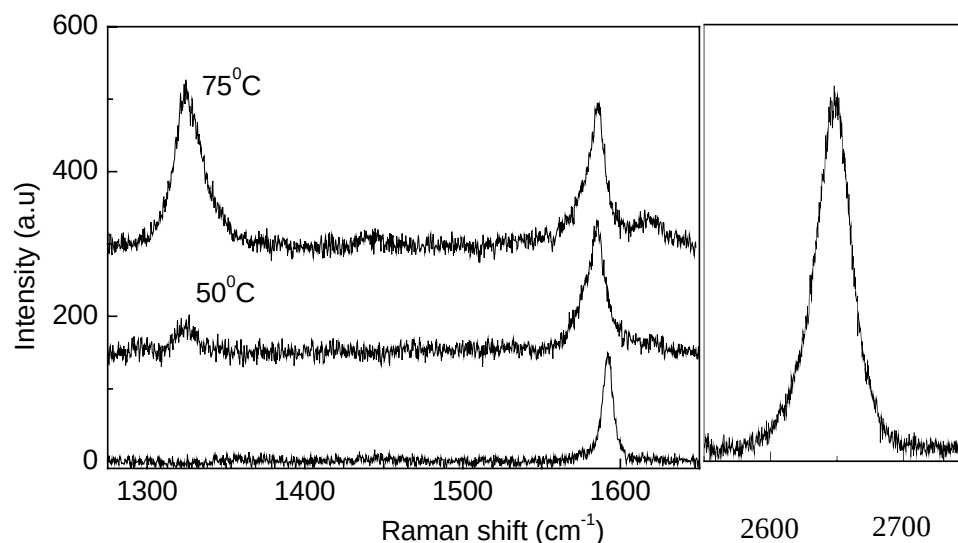


Figure 5.2: *Left panel:* Raman spectra of graphene before (bottom spectrum) and after reaction with BBDT at indicated temperatures. The appearance of D band indicates defect formation in graphene. *Right panel:* Raman 2D band of graphene before functionalization. Its single, sharp Lorentzian lineshape confirms single layer graphene was used in the experiments.

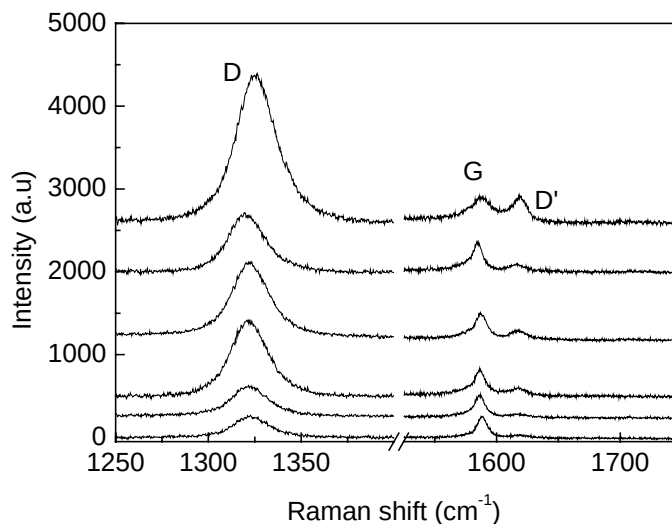


Figure 5.3: Raman spectra at different positions on graphene surface. D band appears at every spots and D- to G-band integrated intensity ratio varies from spot to spot. The top spectrum was collected at graphene edge and it exhibits highest degree of defect, indicating high reactivity of graphene edge.

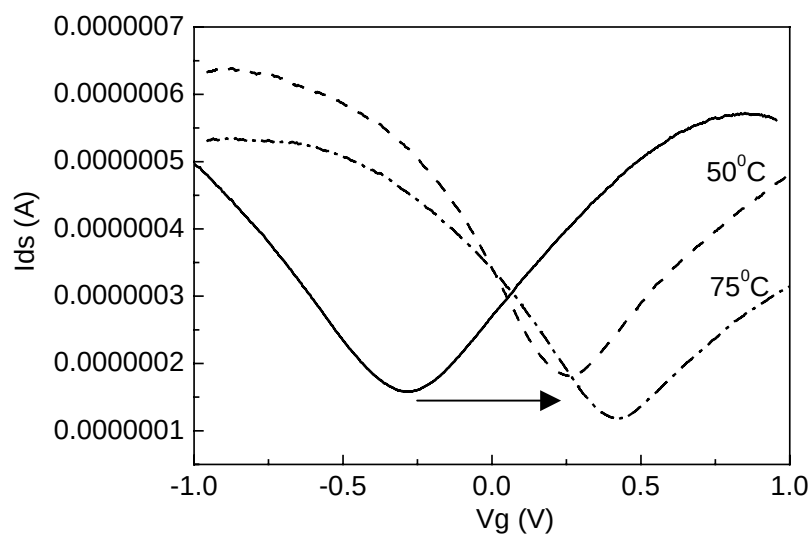


Figure 5.4: Transfer characteristic of graphene device before and after reaction with BBDT at indicated temperatures, corresponding to figure 5.2. 4-BBDT exposure does not significantly alter the current at the neutrality point (the minimum current) or drastically change the gate dependence of the device. There is only a positive shift of DP after the reaction, indicating p-type doping from BBDT as expected [21].

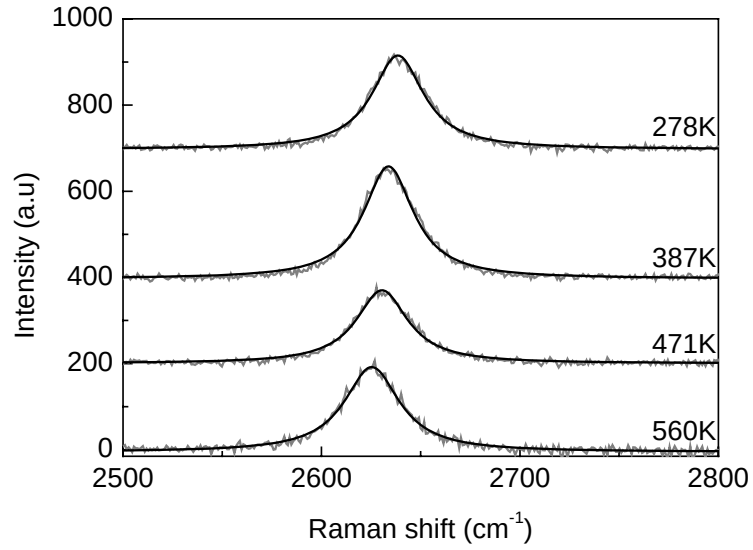
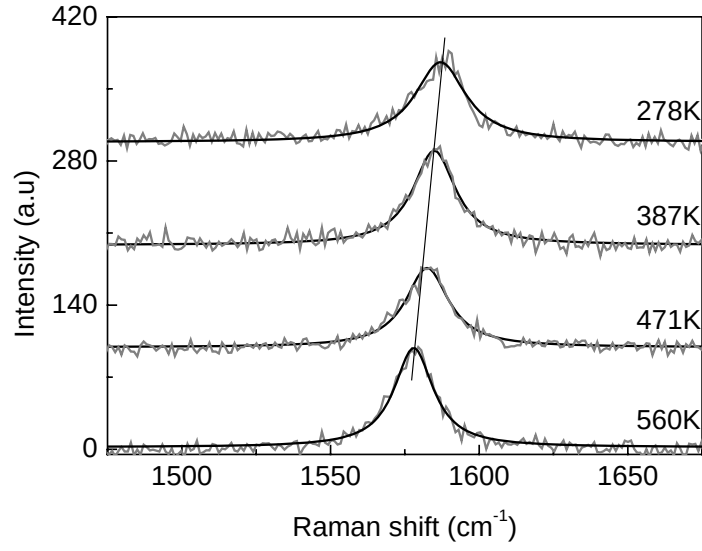


Figure 5.5: Raman G band (upper) and 2D band (lower) of graphene at indicated temperatures and all spectra are collected when the Fermi level is at the DP. Frequency redshift is obvious for both features. The solid line guides the eyes.

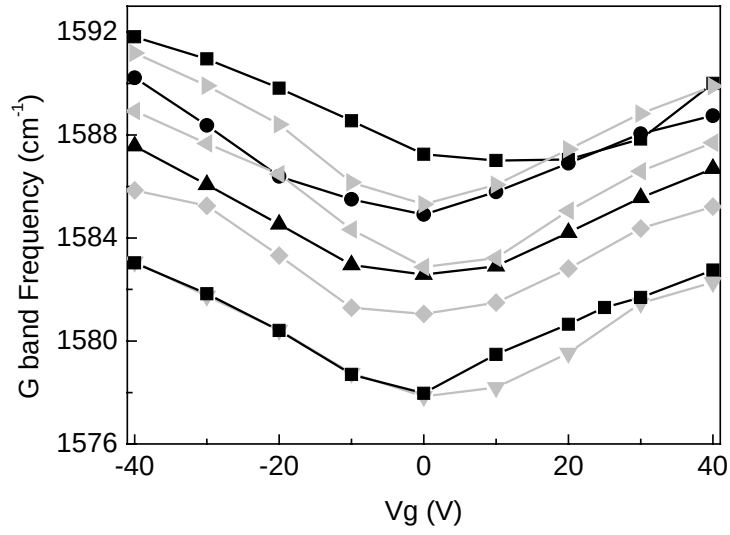


Figure 5.6: Gate dependence of G band frequency at different temperatures: 298 K, 387 K, 471 K, and 560 K (from top to bottom curve) and during the first (black) and second (gray) heating process. The softening of G band phonon when the Fermi level is near the DP due to the presence of Kohn anomaly occurs at all four temperatures.

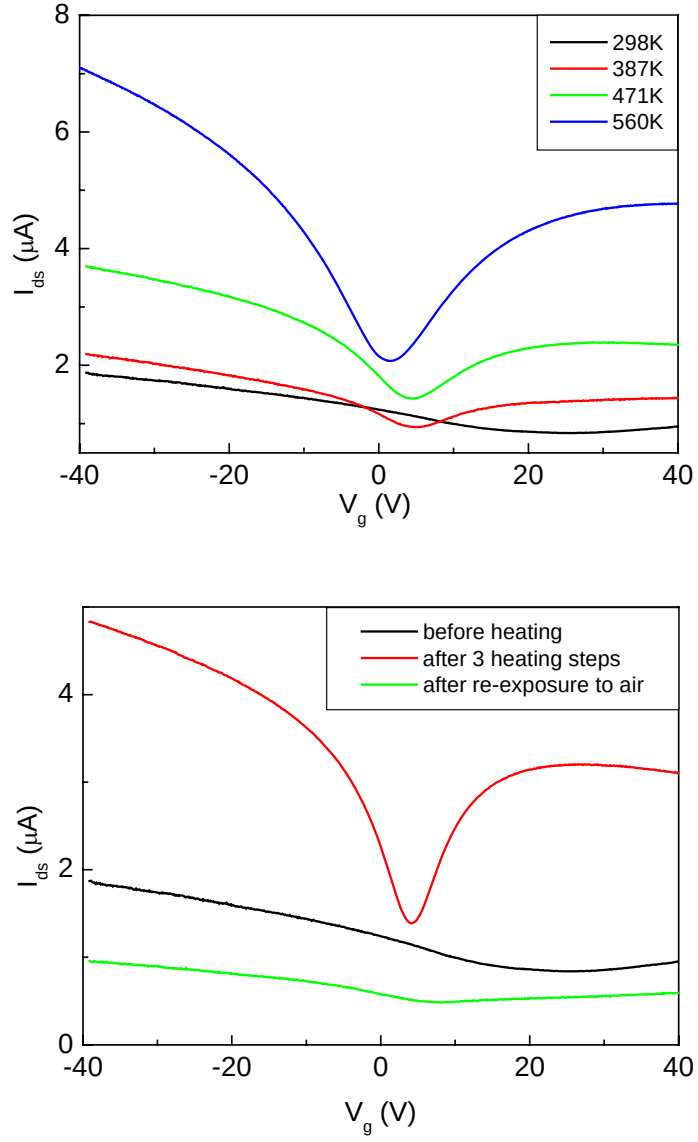


Figure 5.7: Gate dependence of source-drain current at indicated temperatures (upper) and at room temperature before and after heating steps, and after re-exposure to air for 4 days (lower). The observed changes are indicative of reduction of p-type doping by thermal removal of oxygen from the sample. The increasing of source-drain current upon temperature rise is due to better contacts and removal of adsorbed molecules upon Ar annealing.

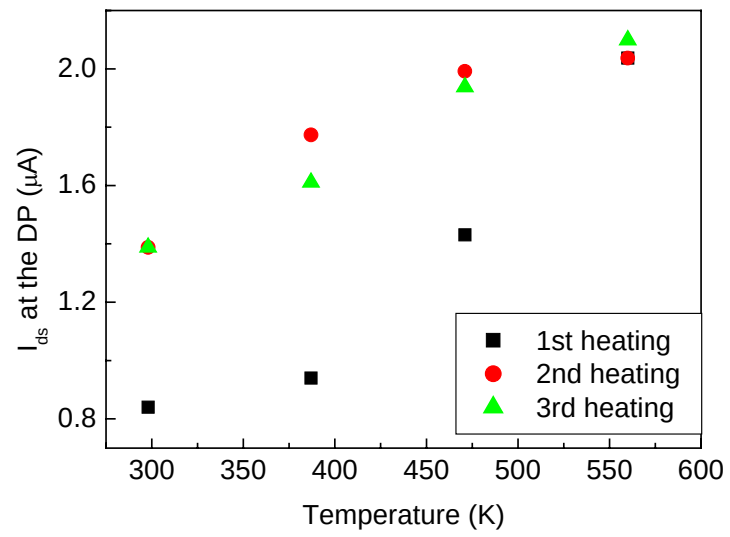


Figure 5.8: Source-Drain current at the DP of graphene device during the first, second, and third heating steps as a function of temperature.

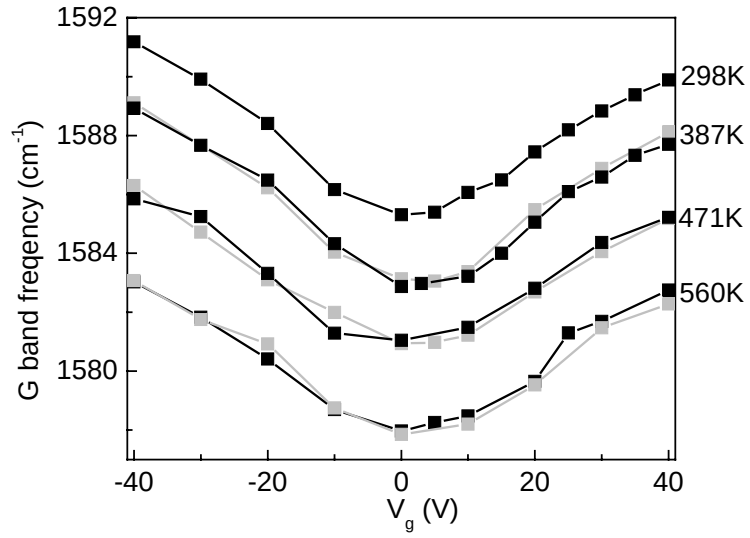


Figure 5.9: The repetition of gate dependence of G band frequency at indicated temperatures during the subsequent cooling (black) and heating (gray) processes after the first heating.

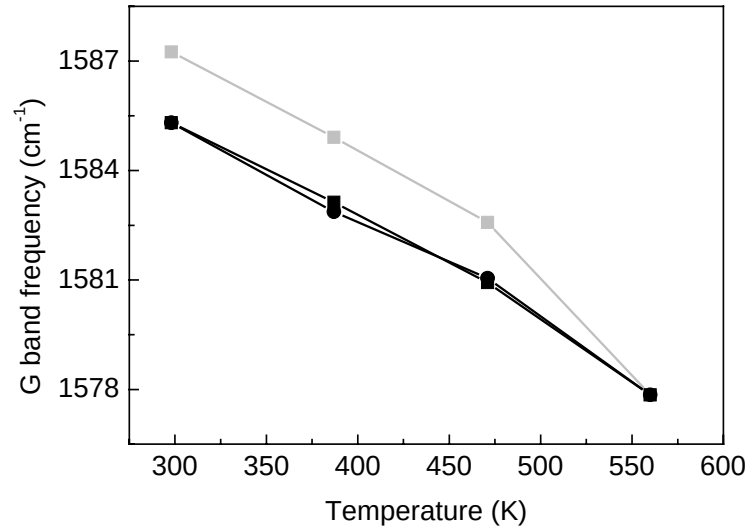


Figure 5.10: Temperature dependence of G band frequency at zero gate voltage when the Fermi level is at the DP during the second (black dots) and third heating steps (black squares) and when it is not ensured (gray).

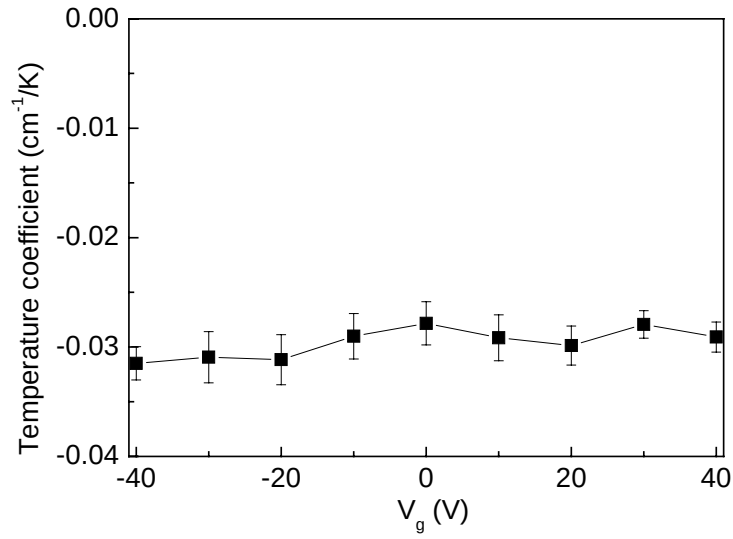


Figure 5.11: Temperature coefficient of G band frequency remains almost independent of gate voltage, indicating the minor role of electron-phonon coupling.

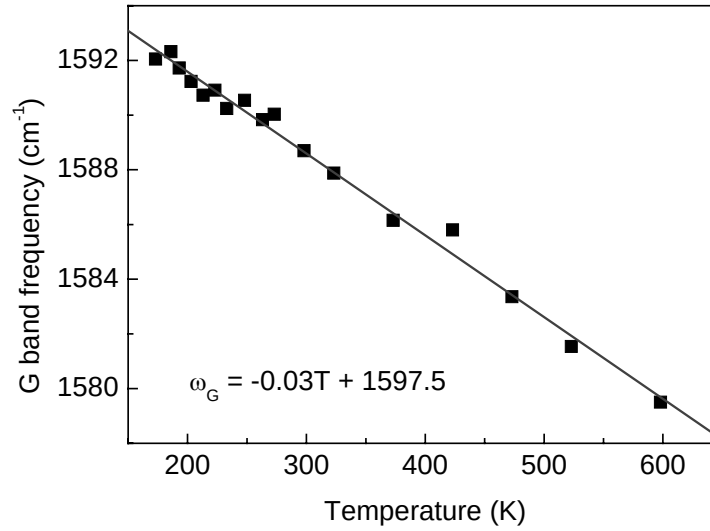


Figure 5.12: Temperature dependence of G band frequency of graphene at the DP. The same value of temperature coefficient α , $-0.03 \text{ cm}^{-1}/\text{K}$, confirms the previous result extracted from figure 5.10.

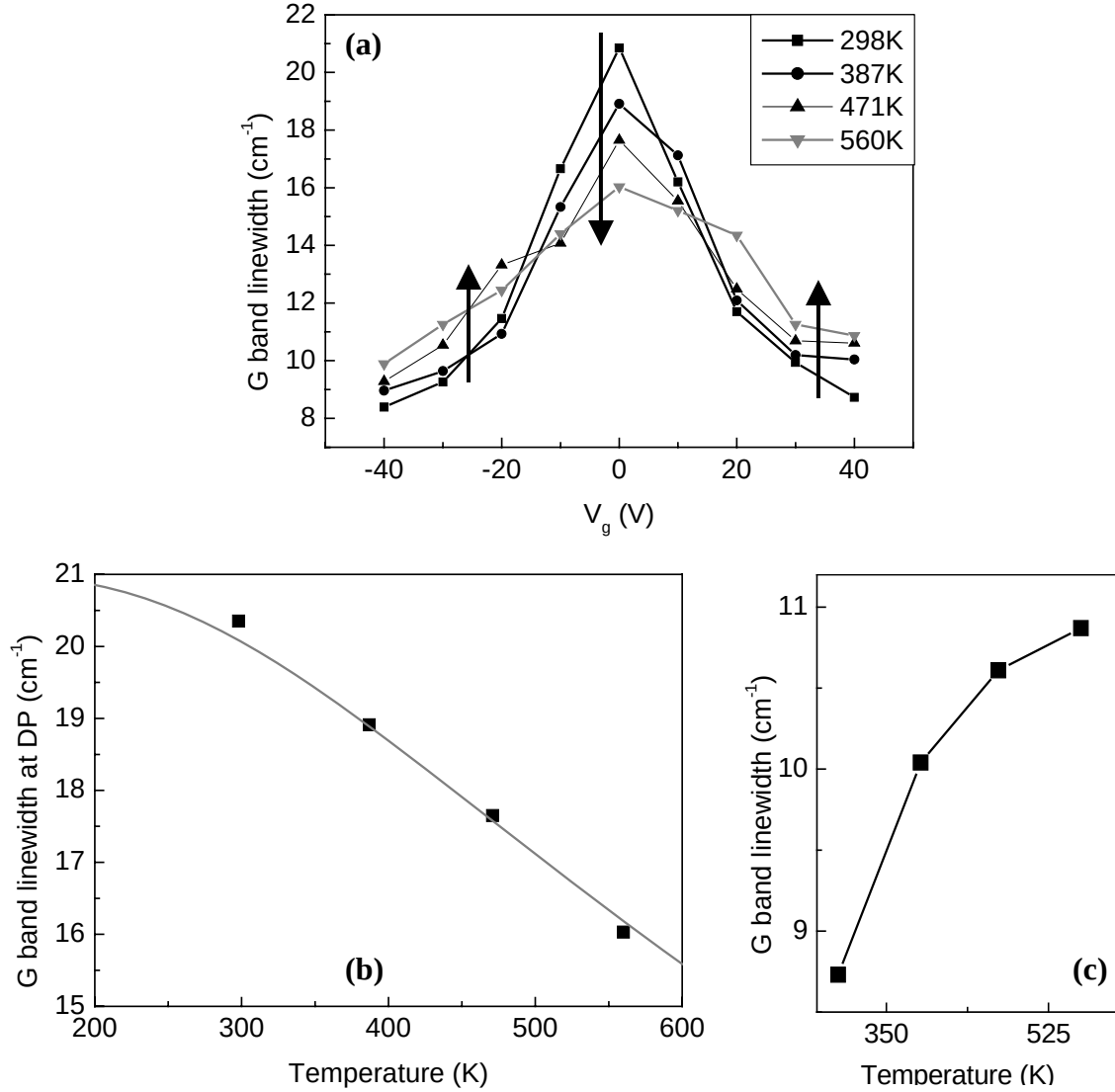


Figure 5.13: (a) Gate dependence of G band linewidth at indicated temperatures. The arrows represent the temperature dependence at different Fermi levels. (b) The decrease of G band linewidth at neutral charged state upon temperature rise with fitted curve obtained from reference 31. (c) The increase of G band linewidth at $V_g = 40$ V where Fermi level is well above the DP because electron-phonon coupling is weakened and phonon-phonon interaction becomes more important.

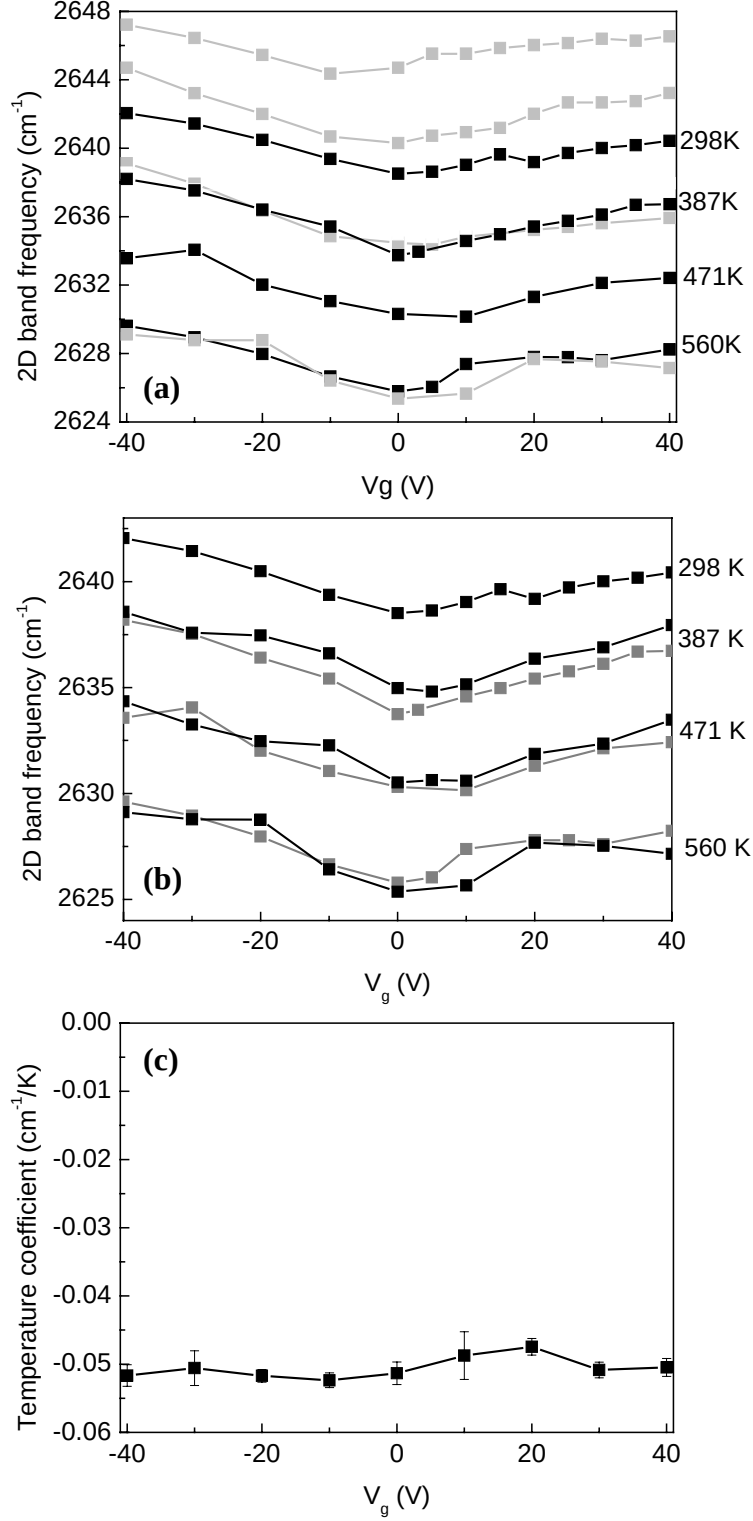


Figure 5.14: Gate dependence of 2D band frequency during the first (gray) and second heating steps (black) (a) and the second and third heating steps (b) and of temperature coefficient of 2D band frequency (c). The temperature coefficient of 2D mode is $-0.05 \text{ cm}^{-1}/\text{K}$ and also nearly independent of gate voltage.

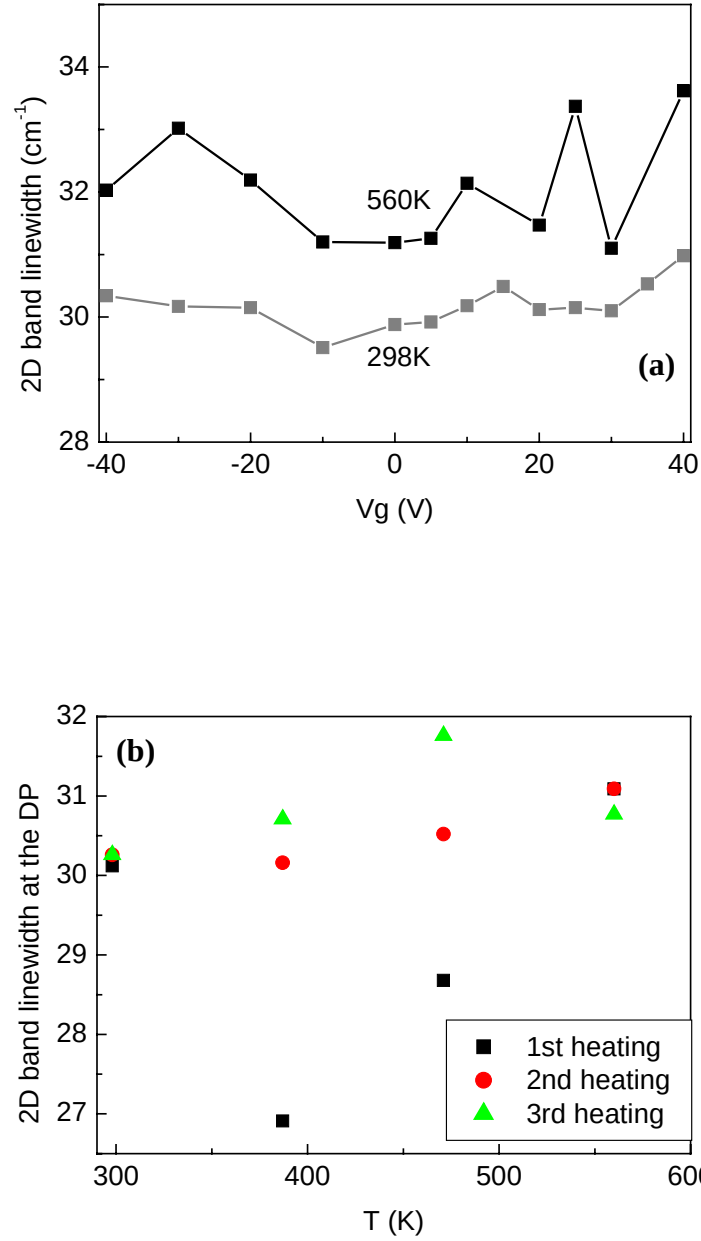


Figure 5.15: The dependence of 2D band linewidth on gate voltage at 298K and 560K (a) and on temperature during several heating steps (b). 2D band linewidth broadens upon heating as expected from phonon-phonon interaction. However, it broadens only 2 cm⁻¹ from room temperature to 560K.

CHAPTER 6

CONCLUSIONS

Single-Walled Carbon Nanotubes (SWCNTs) have been one of the most intensively studied materials. Although it is the wide range of applications of CNTs that attracts most of the media limelight, SWCNTs themselves offer unique opportunity to explore fundamental science of quasi-1D conductors and semiconductors. In addition, because of their single-atomic-layer structure, SWCNTs are extremely sensitive to environmental interactions of which charge transfer and defect formation are the most notable effects. Among a number of microscopic and spectroscopic methods, Raman spectroscopy is a widely used technique to characterize physics and chemistry of CNTs. By utilizing simultaneous Raman and electron transport measurements along with polymer electrolyte top gating, this dissertation focuses on studying charging and defects in metallic (chapters 2 and 3) and semiconducting (chapter 4) SWCNTs at the single nanotube level. These studies have also been investigated in single layer graphene, the building block of SWCNTs, and have been discussed in chapter 5 of this work.

Electron-phonon interaction is critical for several important properties of CNTs, including electrical transport, superconductivity, and optical transitions. The interaction between electrons and phonons is also important factor in Raman scattering, affecting Raman intensity, frequency, and linewidth. In turn, inelastic scattering can measure electron-phonon coupling. Among various Raman features of SWCNTs, the broad and asymmetric Fano lineshape in Raman G band has received much attention as it gives rise to a striking difference between G band feature of semiconducting and metallic SWCNTs. Being able to control charging degree in metallic SWCNTs, the evolution of the G band spectra of single metallic SWCNTs with Fermi level shift has been examined. Appearance of broad and asymmetric peak (LO phonon spectrum) at the Dirac point

indicates that the Fano component is intrinsic to single metallic SWCNTs and arises from coupling between phonon and real vertical electronic excitations (or Kohn anomaly). The Fermi level shift far away from the Dirac point changes the Fano lineshape to narrow Lorentzian as there are no longer electronic states available for proper momentum and energy changes in the electron-phonon scattering. Therefore, while the Fano lineshape is a signature of metallic SWCNTs with the Fermi level close to the Dirac point, Lorentzian is not necessarily indicative of semiconducting SWCNTs. Furthermore, all G modes soften and broaden at the Dirac point, not only the LO mode as predicted by theoretical calculation, and this has been discussed in light of defect formation.

While G band softening is symmetric for electron and hole doping, defect related D-band shows monotonic dependence on the Fermi level shift. Electron-phonon interaction plays a minor role for the D-band phonon. D-band frequency decreases when electrons are injected into the antibonding states, resulting in an expansion of C-C bonds, and increases when holes are injected to bonding states, causing bond contraction. Although charging dependence of G-band and D band are different, the D-to G-band integrated intensity ratio is indicative of defect degree in SWCNTs. Therefore the broadening of G band at the Dirac point needs to be taken into account in order to validate the use of the ratio for metallic SWCNTs.

By systematically introducing covalent defects by reaction with 4-bromobenzene diazonium tetrafluoroborate at different concentrations, we have examined how electrical characteristics and charging dependent Raman G-band phonon softening in individual metallic SWCNTs are influenced by defect formation. In addition to decreasing electrical conductance with increasing on/off current ratio eventually leading to semiconducting

behavior, adding covalent defects reduces the degree of softening and broadening of longitudinal optical (LO) phonon mode of the G-band near the Dirac point. On the other hand, the transverse optical (TO) mode softening is enhanced by defects. Softening of both LO and TO modes may be expected due to covalent defects changing hybridization of C atoms from sp^2 to sp^3 resulting in longer average bond lengths. However, LO mode exhibits stiffening rather than softening because it is already softened via coupling of the phonon with conduction electron excitations and the removal of this effect is the dominant change. These observations imply that reported experimental LO mode frequencies may be higher than the intrinsic frequencies due to the presence of physical disorder, which is observed via measurable D-band intensities in majority of individual metallic SWCNTs.

Raman spectroscopy is utilized as a metrology tool not only for metallic SWCNTs but also for semiconducting SWCNTs. LO phonon in semiconducting SWCNTs also softens when the Fermi level is between the first two van Hove singularities (vHs). This process occurs by phonon-virtual electron hole-pair excitation coupling, unlike metallic SWCNTs where actual carrier excitation occurs. In addition, LO linewidth broadens significantly near vHs, in contrast with the narrowing in metallic nanotubes and with theoretical prediction. The linewidth increasing is possibly inhomogeneous broadening due to spatial difference of charge density. Charging dependence of LO mode remains nearly unchanged upon introduction of covalent defects formed through reaction with 4-bromobenzene diazonium tetrafluoroborate.

Doping single layer graphene, the building block of SWCNTs, by chemical and electrostatic means has also been discussed in chapter 5 of this dissertation. The former is

carried out also by using 4-bromobenzene diazonium tetrafluoroborate. While 4-BBDT causes p-doping of graphene, it does not help to open an electronic gap as in metallic SWCNTs. Different reaction conditions or functional groups are recommended to introduce a bandgap in graphene. Electrostatic doping of graphene at different temperatures demonstrates the importance of ensuring the Fermi level in studying temperature dependence of G band frequency. It also has been shown that contribution of electron-phonon coupling to G peak position shift upon temperature change is negligible and phonon-phonon interaction is dominating the line shift.

In short, simultaneous Raman spectroscopy and electrical measurement has been proven to be a powerful combination of characterization techniques in studying SWCNTs and graphene. It has revealed several important physical properties of the 1D and 2D materials. Furthermore, it has helped to established background for potential carbon-based electronic applications. The results described in this dissertation contribute to progress in realizing carbon-based electronics.