AN ABSTRACT OF THE DISSERTATION OF

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CNTs also offer new opportunities to study new science and develop new technology enabled by their strong electron-electron (e-e) interactions. The lack of dielectric screening inherent in nanoscale structures like CNTs leads to strong e-e interactions, which produce unique physical phenomena. In this thesis, we study the effects of strong e-e interactions in CNTs through the experimental system of suspended CNT devices fabricated with two gate electrodes. The work presented here includes the development of a theoretical framework to understand of the behavior of these 'split-gate' devices. Using this framework, we are able observe signatures of the strong e-e interactions in CNTs.

The purpose of using split-gates (two gate electrodes) is to electrostatically dope the CNT into a pn junction. These suspended CNT pn junctions have been used by several groups to investigate the optoelectronic properties of CNTs. However, the device transport models proposed by previous authors have been unable to explain the disparities in experimental observations. In particular, different authors have seen different responses of the source-drain current vs source-drain bias (I_{sd} - V_{sd} characteristic) of similar devices. To explore the reason for this variability, we investigate the I_{sd} - V_{sd}

characteristic while varying the metal contact work function. The results allow us to develop a model that explains the variation in the literature in terms of variations in the metal work functions and/or CNT diameter. The device is modeled with a pn junction diode in the center of the CNT and Schottky diodes at the contacts. We are also able to use this model and temperature dependent measurements to extract the n-type and p-type Schottky barrier heights.

Carbon nanotubes (CNTs) are a promising material for high-performance electronics beyond silicon. Unlike silicon, the nature of the transport band gap in CNTs is not fully understood. The transport gap in CNTs is predicted to be strongly driven by e-e interactions and correlations, even at room temperature. The effects a dielectric material, like a SiO₂ substrate, on the transport gap is important for implementation of this technology. Here, we use dielectric liquids to screen e-e interactions in individual suspended ultra-clean CNTs. Using multiple techniques, the transport gap is measured as dielectric screening is increased. Changing the dielectric environment from air to isopropanol, we observe a 25% reduction in the transport gap of semiconducting CNTs, and a 32% reduction in the band gap of narrow-gap CNTs. Additional measurements are reported in dielectric oils. Our results elucidate the nature of the transport gap in CNTs, and show that dielectric environment offers a mechanism for significant control over the transport band gap.

CNTs are candidates for next-generation photovoltaic technology, because they have the potential to break the Shockley-Queisser limit. Because of the strong e-e interactions, photogenerated carriers in CNTs can undergo carrier multiplication, where more than one electron-hole pair is created per absorbed photon. The photocurrent quantum yield (PCQY), defined as the number of electron-hole pairs extracted from a device per absorbed photon should therefore be able to exceed unity. However, a previous measurement on a similar split-gate device only achieved PCQY of 1-5%. To address this discrepancy we study photocurrent generation in individual suspended carbon nanotube pn junctions using spectrally resolved scanning photocurrent microscopy. Spatial maps of the photocurrent allow us to determine the length of the p–n junction intrinsic region, as well as the role of the n-type Schottky barrier. We show that reverse-bias operation eliminates complications caused by the n-type Schottky barrier and increases the length of the intrinsic region. We develop a method of determining the PCQY that takes into account the beam waist, length of the intrinsic region, CNT diameter, resonant absorption cross section of CNTs, and intensity enhancement from reflection off the substrate. We find that the room temperature PCQY is approximately 30% when exciting the carbon nanotube at the *S*₄₄ and *S*₅₅ excitonic transitions. The PCQY value is an order of magnitude larger than previous estimates. ©Copyright by Lee Aspitarte

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Electron-Electron Interaction Driven Phenomena in Carbon Nanotube Devices

by

Lee Aspitarte

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Lee Aspitarte, Author

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CONTRIBUTION OF AUTHORS

Daniel McCulley assisted with the suspended CNT split-gate device fabrication in Chapters 3-5 and performed the liquid gated semiconducting CNT measurements of Chapter 4. Gary Steele, Joshua Island, and Marvin Ostermann provided the equipment and assisted with the Coulomb blockade measurements in Chapter 4. Andrea Bertoni performed electrostatics device simulations and Massimo Rontani performed RPA-screened transport gap calculations in Chapter 4. Ethan Minot provided insight, guidance and motivation for all aspects of the work presented in this dissertation.

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Dedicated to Martha

Electron-electron Interaction Driven Phenomena in Carbon Nanotube Devices

CHAPTER 1

Introduction

1.1 Introduction

The unique effects that arise from confining electrons to nanoscale dimensions hold great promise for new scientific and technological paradigms. In this thesis, we explore the effects that arise from the strong e-e interactions present in nanomaterials. In common bulk semiconductors, like the silicon ingots shown in Figure 1.1a, the e-e interactions are weak. Electrons in the crystal have plenty of room to readjust and thereby screen electric fields. The situation is different for nanomaterials like those shown in Figure 1.1b-d. The quantum confinement of electrons in these nanoscale dimensions enhances the e-e interactions, producing unique physical phenomena. The physics of interacting electrons is scientifically important, but we also need to understand these phenomena to implement nanomaterials into next generation technology.



Figure 1.1 Examples of 3D, 2D, 1D and 0D materials. From left to right the dimensionality of the material (number of dimensions with length scales much larger than atoms) decreases. 3D (Silicon): Top shows the crystal unit cell and bottom shows a photograph of Silicon ingots (Image courtesy of Siliconwafer.org). 2D (MoS₂): Top shows an atomic arrangement of MoS₂ and bottom shows an optical microscopy image of a MoS₂ flake on a SiO₂ (purple) substrate.
This flake was achieved through mechanical exfoliation. The bright blue parts indicate multiple layer MoS₂ and the dark blue region is a single atomic layer as measured by atomic force microscopy. 1D (CNT): top shows the atomic structure of a CNT and bottom shows a transmission electron microscopy (TEM) cross section down the axis of the CNT. The TEM image was taken in collaboration with Pinshane Huang. 0D (Quantum Dot): Top shows the atomic structure of a CdS quantum dot and bottom shows a TEM image. TEM image taken from Ref¹.

CNTs (Figure 1.1c) are 1D nanomaterials and are promising candidates for implementation of nanotechnology and exploration of effects of strong e-e interactions. Because of their wire like shape, they have a high degree of quantum confinement, but allow for easy transport and extraction of charge carriers along the CNT axis. Compared to a quantum dot, it is relatively easy to connect electrodes to an individual CNT to probe the effects of e-e interactions.

One technological use for this system, which is explored in this thesis, is high-efficiency conversion of light into electricity. Carrier multiplication, a process that is enabled by strong e-e

interactions, has already been experimentally observed in CNT photodiodes.² Solar cells that utilize carrier multiplication have the potential to surpass the theoretical limit on the power conversion efficiency that applies to existing solar technologies (Section 1.2.3).

CNTs are also a promising technology for reducing the dimensions of transistors. Semiconducting CNTs have already been used as the semiconducting channels of the transistors in a functioning computer.³ The e-e interactions, and turn the electronic properties of CNTs, will be strongly affected by the presence of a dielectric substrate. The dependence of CNT electronic properties on dielectric environment must be understood for a successful implementation of CNTs in computers.

In this introduction, we introduce two themes present in this thesis. In Section 1.2 we discuss why the e-e interactions are strong in nanomaterials, and the effects that arise from these strong e-e interactions. In Section 1.3, we discuss an experimental system that can be used to measure the effects that arise from e-e interactions.

1.2 Electron-electron interactions in CNTs

1.2.1 Strong electron-electron interactions in nanomaterials

One of the hallmark properties of nanomaterials is the strong interactions between charge carriers within them.⁴ Materials exhibiting strong electron-electron (e-e) interactions lead to unique physical phenomena and new technological possibilities. For example, materials with strong e-e interactions can exhibit a metal-to-insulator transition, which may lead to next-generation transistors.⁵ Interactions are also thought to play a central role in high temperature superconductivity.⁶ In this work, we are interested in exploring how the strong e-e interactions present in CNTs could lead to highly efficient next-generation solar technology (Section 1.2.3). We are also interested in how the e-e interactions are affected by the proximity of a dielectric

material (Section 1.2.4). The effect of dielectric environment is interesting from a fundamental standpoint, but also critical to understand before using CNTs in next generation field-effect transistors because the CNTs would lie on a dielectric substrate.

The e-e interactions are strong in CNTs and other nanoscale structures in part because of the lack of dielectric screening. Imagine placing an extra electron within bulk silicon. This electron might have originated from doping, or might have been created in addition to a hole during an optical excitation as in Figure 1.2a. In bulk systems, the other electrons in the material will readjust to the presence of the added electron. In a system with an appreciable carrier density, free holes will accumulate near the extra electron. In wider gap ($E_g > 0.5 \text{ eV}$) intrinsic semiconductors screening can still occur as a polarization of the core electrons (Figure 1.2a).⁷ In either case, the effective charge of the added electron is reduced and the effective strength of the Coulomb interaction is weakened. In nanoscale materials, the dielectric screening is reduced and the e-e interaction. In the absence of a polarizable material, electric field lines leak out into the surrounding air/vacuum environment and the electrostatic interaction between charges is enhanced with respect to bulk materials.



Figure 1.2 Demonstration of the lack of dielectric screening in a nanoscale material. a) An electron-hole pair in a bulk material. The dielectric screening of the material reduces the Coulomb interaction. b) In a nanomaterial, the electric field lines can leak out into the environment and the Coulomb interaction is enhanced. The strength of the electric field is represented by the spacing between the electric field lines.

In addition to reduced dielectric screening, quantum confinement also plays a role in the enhanced e-e interactions. For example, going from a bulk to 2D material, while keeping the dielectric screening unchanged, causes an increase the exciton binding energy of a factor of four.^{4,8} The contribution from confinement can be understood in terms of a "forced overlap" of the electronic wavefunctions.⁹

1.2.2 Transport gap and optical gap

The strong e-e interactions present in CNTs will affect their electronic transport and optical properties. The electronic transport properties are related to the transport bandgap, E_g , which is defined as the energy required to move an electron from the valence band to the conduction band.^{10,11} E_g is therefore the relevant energy, for example, to describe the splitting of p-type and n-type threshold voltages when a CNT is used as a semiconducting channel in a field-effect transistor (Section 3.4).¹² E_g will also determine the energy barrier relevant for electronic transport in a pn junction.¹³ The optical properties will be related to the optical bandgap, E_{opt} ,

which describes the energy required to create an electron-hole pair upon absorption of a photon.^{10,11}

In a non-interacting picture, $E_g = E_{opt} = E_{g,bare}$, where $E_{g,bare}$ is the 'bare' bandgap, i.e. the bandgap without e-e interactions. In other words, there is no difference between creating an electron and hole separately or together, because the electron and hole do not interact with each other. This situation corresponds to the familiar case of bulk semiconductors. For example, the absorption onset and electronic properties of silicon are both described by the same bandgap $E_g = E_{opt} = 1.1$ eV. With the addition of e-e interactions, this equivalency is no longer true and $E_g \neq E_{opt}$.

Figure 1.3 shows the relationship between $E_{g,bare}$, E_{opt} , and E_g for a system with e-e interactions. With the addition of e-e interactions, E_g is increased by the self-energy, Σ . This increase in energy arises from electrostatic repulsion.¹⁴ Optical excitations create electron-hole pairs, which can be bound as excitons by the strong coulomb interaction. The energy required to create an exciton, E_{opt} , will be less than E_g by the exciton binding energy (E_b). To summarize, $E_g = E_{g,bare} + \Sigma$ and $E_{opt} = E_g - E_b$.



Figure 1.3 The relationship between $E_{g,bare}$, E_{opt} , and E_g for a system with e-e interactions.

Interestingly, e-e interactions increase both Σ and $E_{\rm b}$ which gives rise to an optical gap that is not strongly dependent on the strength of e-e interactions.¹⁵ In Section 1.2.4 we discuss how the e-e interaction strength can be tuned by immersing a CNT in a dielectric environment. Indeed, measuring the optical spectra of CNTs immersed in materials with a wide range of dielectric constant results in only in small fractional shifts (~5%) of the optical transition energies.¹⁶ On the other hand, $E_{\rm g}$ should have a much stronger dependence on e-e interaction strength and in Chapter 4 we directly measure this strong dependence.

In the rest of this thesis, we refer to the optical gap as the excitonic transition or excitonic resonance. In addition to excitonic resonances, higher energy optical transitions exist. The simplest is a band-to-band transition corresponding to the formation a well-separated electron and hole, which requires a photon energy equal to the transport bandgap. Other optical transitions can arise from interactions with phonons¹⁷ and higher-order excitonic transitions.^{4,18}

1.2.3 Carrier multiplication

Strong e-e interactions affect the energy relaxation pathways of photogenerated carriers, which has exciting potential for increasing the power conversion efficiency (PCE) of photovoltaic technology. The PCE of single-junction solar cells currently under commercial production, which utilize bulk semiconductors, is asymptotically approaching a theoretical limit called the Shockley-Queisser (SQ) limit. The SQ limit is a limit on the PCE of single junction solar cells of about 33%.¹⁹ State-of-the-art silicon solar cells, for example, have a power conversion efficiency of approximately 25% after decades of optimization.

One of the assumptions used in the derivation of the SQ limit is that each absorbed photon results in no more than one electron harvested from the device. Specifically the photocurrent quantum yield (PCQY),

$$PCQY = \frac{e^{-} Harvested}{Photons Absorbed} , \qquad (1.1)$$

is assumed to less than or equal to 1. This is a good assumption for solar cells that are fabricated with bulk semiconductors. However, the strong e-e interactions in nanomaterials allow for solar cells with PCQY > 1 that can break the SQ limit.

The relationship between the SQ limit and PCQY ≤ 1 is illustrated in Figure 1.4. This figure uses the example of silicon as the semiconductor absorber, which has a bandgap $E_g = 1.1$ eV. Photons with energy lower than the bandgap are shaded red and will not be absorbed, representing an immediate loss in PCE. Electrons created from photons with higher energies than the bandgap of the semiconductor absorber will quickly relax to the band edges. For clarity, we will describe the relaxation dynamics of electrons, but the same processes occur for holes. Because the electrons do not interact, high-energy electrons can only lose their extra energy by interacting with the atomic cores, creating heat in the form of lattice vibrations (phonons). Therefore, the electrons that relax to the conduction band edge only retain a fraction E_g/E_{ph} of the photon energy. The blue shading represents the thermal loss of the extra energy contained within these high-energy photons. Additional energetic losses, represented by the black shading, result from radiative recombination and impedance matching (i.e. a maximum value for the fill factor). In the end, the result is that 33% of the power contained within the solar spectrum can be converted into electric power.



Figure 1.4 Visualizing the Shockley-Queisser limit with the solar spectral irradiance. a) The solar spectral irradiance at the surface of the earth (AM 1.5).²⁰ The graph is colored with respect to the bandgap of silicon ($E_g = 1.1 \text{ eV}$, see inset). b) A schematic of the relaxation of a high-energy electron-hole pair in a system with and c) without CM.

In a system with strong e-e interactions, it is possible to harvest some of the thermal loss (blue shading, Figure 1.4) through the process of carrier multiplication (CM). During CM, electrons created from photons with energies at least twice as large as the bandgap of the semiconductor absorber can relax by exciting extra electron-hole pairs across the bandgap, instead of emitting phonons. Therefore, CM enables a PCQY > 1. The limit on PCE for a photovoltaic device that exhibits CM is 43%.²¹ Achieving this PCE requires that CM is efficient, meaning that high-energy photons excite as many electron-hole pairs across the bandgap as are allowed by conservation of energy. Mathematically, efficient CM is described by PCQY = $\left[\frac{E_{ph}}{E_g}\right]$, where $\lfloor x \rfloor$ denotes the floor operation (rounding down to nearest integer).²²

CM is very inefficient in bulk semiconductors because of the weak interactions between electrons. CM does occur, but only for very high photon energies. For example, the onset of CM in silicon is $E_{\rm ph} \sim 7E_{\rm g}$.²³ Because the solar irradiance is negligible at these photon energies, CM arising from these photons cannot make significant impact to the PCE. PCQY > 1 has been achieved in quantum dot¹¹ and nanorod¹² solar cells for lower photon energies ($E_{\rm ph} \sim 3-4E_{\rm g}$). However, efficient charge extraction remains a challenge for solar cells fabricated from these 0-D materials and PCQY > 1 was only achieved by optimizing the solar cell for absorption of high photon energies. The PCQY < 1 for most of the solar spectrum and the resulting PCE was only a few percent.

CNTs are attractive nanomaterials for exploring CM. The 1-D structure of CNTs allows for easy contact to metal electrodes and efficient charge extraction. In addition, efficient CM has already been observed CNT photodiodes, with an onset of CM occurring at $E_{ph} = 2E_g$.² However, the authors were only able to infer that CM was occurring and could not measure the PCQY. Developing a method of measuring and optimizing the PCQY in CNT pn junctions is one of the main results of this thesis (Chapter 5).

1.2.4 Dielectric screening

The fact that the e-e interactions are enhanced by a lack of dielectric screening (Section 1.2.1) implies that the proximity of a dielectric material could affect the e-e interactions. The sensitivity of CNTs to dielectric environment is particularly important because CNTs are candidates for the semiconducting channels of next-generation field-effect transistors.³ In this application, CNTs would likely lie on a dielectric substrate such as SiO₂. Understanding the effect of this dielectric on the electronic properties of the CNT will be critical to their successful implementation. Sensitivity to dielectric environment also may allow for the tailoring of physical properties to various applications.

Figure 1.5a illustrates the sensitivity to dielectric environment by showing a bound electron and hole interacting in a CNT with and without the presence of a dielectric environment. In a vacuum environment, the electric field lines leak out into the vacuum and lead to a strong e-e interaction. When the same CNT is lying on a dielectric substrate (Figure 1.5b), some of the field lines will permeate into the substrate. In this situation, some of the dielectric screening will be reintroduced and the e-e interaction will be reduced. Experimentally, we use dielectric liquids as the screening material instead of dielectric substrates as shown in Figure 1.5c (Section 4.3). Dielectric liquids allow for switching between dielectrics, fully surrounding the CNT, and do not have the complicating effect of electrostatic disorder. In Chapter 4 we immerse CNTs in dielectric liquids and measure how changing the e-e interaction strength affects electronic properties of the CNT.



Figure 1.5 A bound electron-hole pair in CNTs with different dielectric environments. The lines represent electric field lines. The electric field strength, represented by the density of the electric field lines, decreases in a dielectric. The strength of the screening depends on how surrounded the CNT is and the dielectric constant surrounding material.

1.3 Electrically-contacted CNTs to study e-e interactions

Researchers have used many different experimental paradigms to explore the interesting CNT physics outlined so far. For example, in the infancy of CNT research purely optical characterization techniques such as photoluminescence spectroscopy were widely used to study CNTs.²⁶ The non-contact nature of these methods allowed for the simultaneous investigation of large ensembles of CNTs, and no need for device fabrication. However, purely optical

measurements have their shortcomings. For example, it is difficult to explore the physics of e-e interactions through optical methods because the optical resonances are not strongly affected by dielectric environment (Section 1.2.2). To measure effects like the strong dependence of E_g on dielectric environment, we require electrical contacts to the CNT.

To study the electronic and optoelectronic properties of electrically-contacted CNTs we fabricate the suspended CNT split-gate device shown in Figure 1.6. The details of these devices are presented in Chapter 3. Briefly, a CNT is grown across a trench to connect to two metal electrodes, called source and drain electrodes. Electrically connecting to the source and drain electrodes allows us to push current through the device by applying a bias, or monitor the current generated from illuminating the device. Underneath the CNT are two gate electrodes that are used to electrostatically dope the CNT, and can operate the device as either a field-effect transistor, diode, or photodiode. We utilize these different 'modes' to both study different aspects of the intrinsic physics of CNTs and explore the potential of CNTs for use in those technological applications. For example, operating the device as a photodiode, we can study the interesting physics of carrier multiplication while simultaneously learning how to achieve a PCQY > 100% in a real photodiode. In fact, the pristine and suspended nature of the CNT means that we are measuring how CNTs behave in devices without the complicating factor of a dielectric substrate or photolithography residues.



Figure 1.6 The CNT split-gate device. a) 3D rendering of the CNT split-gate device. All dimensions are to scale except for the CNT. b) Scanning electron microscopy image of a CNT split-gate device where a CNT can be seen connecting the source and drain electrodes.

To use these devices to probe the physics of interacting electrons, we need to understand their response to external stimuli such as the application of a source-drain voltage or illumination with light. To achieve this, it is not enough to know just the physics of an isolated CNT. We have understand the physics of the entire CNT/metal electrode system. How electrons enter and exit the CNT from the metal electrodes? What voltages should be applied to the various electrodes to optimize the extraction of photogenerated charges?

In Sections 1.3.1- 1.3.3, we introduce the basic concepts of semiconductor device physics, which will be used to answer the above questions. The following is a general discussion that applies equally to bulk semiconductor devices as well as nanoscale devices. The device physics specific to CNT split-gate devices is presented in detail in later chapters. The electronic transport is discussed in Chapter 3 and the optoelectronic properties are discussed in Chapter 5.

1.3.1 Electrostatics of semiconductor interfaces

A semiconductor device must have a semiconductor interface. For example, in a solar cell there must be metal electrodes connected to the semiconductor absorber to extract the photogenerated charges. The importance of the interfaces in semiconductor devices is well summarized by Nobel laureate Herbert Kroemer who famously said "The interface is the device".²⁷

Drawing a band diagram is the basic method of understanding the behavior of semiconductor interfaces. In Figure 1.7, the basics of band diagrams are presented through the example of perhaps the most well-known semiconductor interface, the pn junction. The pn junction, as the name implies, is the interface between a p-doped semiconductor and n-doped semiconductor. Figure 1.7a shows the band diagram of an isolated p-type and n-type semiconductor. The two semiconductors are characterized by their work functions (WF), defined as the difference between the Fermi level and the vacuum level. The vacuum level is the energy of an electron just outside the material, and will be proportional to the electrostatic potential.¹¹



Figure 1.7 Forming the band diagram of a pn junction. A p-type and n-type semiconductor are shown a) before and b) after contact. E_c and E_v refer to the edges conduction and valence bands of the semiconductor, respectively. $E_{f,n}$ and $E_{f,p}$ are the Fermi levels (electron chemical potentials) of the n-type and p-type semiconductors, respectively. The difference in the WFs of the semiconductor leads to a built in potential difference, V_{bi} , and a transport barrier, Φ_0 (shown for holes in the diagram). The light gray shading represents unfilled states and the dark gray

shading represents filled states.

Because of the difference in WFs, electrons have a lower energy in the p-type semiconductor than the n-type semiconductor. Upon contact, electrons will transfer from the n-type to p-type semiconductor through recombination with holes (Figure 1.7a). The region between the p-type and n-type semiconductors becomes depleted of charge carriers and is thus called the depletion or intrinsic region. This charge transfer creates a charge dipole and therefore a change in the electrostatic potential (or vacuum level) across the intrinsic region. In contrast to the electrostatic potential, the Fermi level is constant throughout the junction, as is necessary for a system in thermal equilibrium.

The magnitude of the electrostatic potential drop is called the built in voltage, $V_{bi} = WF_p - WF_n$. The conduction and valence bands will bend an amount V_{bi} . However, the probability that a carrier will be able to cross the pn junction is defined with respect to the Fermi level, not the band edges. The actual transport barrier, Φ_0 , includes the separation of the Fermi level from the band edges. i.e. $\Phi_0 = V_{bi} + (E_f - E_c)$ for electrons and $\Phi_0 = V_{bi} + (E_f - E_v)$ for holes. Φ_0 represents the potential energy barrier that carriers must overcome to flow through the system. The built in voltage leads to electrical rectification (diode behavior) as well as provides an electric field that can separate photogenerated charge carriers (photodiode behavior).

Metal-semiconductor junctions are another ubiquitous interface in semiconductor devices. Current must be injected or extracted from the device via metallic electrodes. The CNT split-gate device, for example, has two metal contacts. Figure 1.8 shows a p-type semiconductor before and after contact with a metal electrode. In this example, the WF of the metal is greater than that of the CNT. Therefore, electrons in the CNT will transfer into the metal upon contact. The analysis is very similar to a pn junction and the transfer of charge between the two materials will again create an energetic barrier. In the case of a metal-semiconductor junction, this energetic barrier is called a Schottky barrier, and Φ_0 is called the Schottky barrier height. In the case of the p-type Schottky barrier of Figure 1.8, $\Phi_0 = V_{bi} + (E_f - E_v)$, similarly to the pn junciton. This equation can be alternatively written $\Phi_0 = WF_M - IP_{CNT}$, where IP_{CNT} is the ionization potential of the CNT, defined as the difference between the valence band and vacuum level.



Figure 1.8 Forming the band diagram for a metal-semiconductor junction. The metalsemiconductor junction is also called a Schottky junction.

The equation $\Phi_0 = WF_M - IP_{CNT}$ implies that the Schottky barrier height should vary directly with the metal work function. This relationship is known as the Schottky-Mott model of metal semiconductor interfaces, which turns out to often be inaccurate in bulk semiconductor devices. In reality, Φ_0 is experimentally insensitive to the metal work function for bulk semiconductormetal junctions.²⁸ This was originally explained by Bardeen in terms of dangling bonds at the surface of the semiconductor, which store charge and 'pin' the Fermi level within a certain position of the bandgap, regardless of the metal work function.²⁹ In general, quantum states with energies within the semiconductor bandgap can arise at the interface from various mechanisms.³⁰ These gap states fill or empty in response to changes in the contact metal (and therefore metal
WF). This transfer of charge leads to a surface dipole that effectively screens the semiconductor from changes in the metal WF.

Unlike conventional semiconductor devices, the WF of the metal contacts has been shown to dramatically affect the behavior of CNT devices.³¹ In fact, Fermi level pinning is theoretically predicted to not have a significant effect on the characteristics of CNT devices.³² In a bulk semiconductor device, the surface dipole arising from Fermi level pinning is planar and therefore affects the electrostatic potential an infinite distance away from the interface. In a 1D system like a CNT, the interface charge is confined to a line normal to the interface. The potential generated by the interface charge dies off much more quickly with distance. The dipole therefore does not end up affecting Φ_0 . In addition, defect states, which are a common cause of Fermi level pinning, should not exist in our pristine CNTs. Therefore, suspended CNT split-gate devices should have outstanding sensitivity to the metal WF. In Section 3.5, we demonstrate the remarkable sensitivity of CNT-metal Schottky barriers to the metal WF.

1.3.2 Effect of source-drain bias

We now consider the effect of applying a source-drain bias across the pn junction and Schottky junctions. Figure 1.9 shows band diagrams for both a pn junction and Schottky barrier under an applied source-drain voltage (V_{sd}). We are interested in the current that will flow between the source and drain electrodes, I_{sd} , for a given V_{sd} . In the following, we derive the basic form of I_{sd} (V_{sd}). Rigorous derivations can be found in references ³³ and ³⁴, which this section heavily draws upon.

To arrive at an expression for $I_{sd}(V_{sd})$ consider the balance between left and right moving holes that are incident on the junction. The holes will encounter an energetic barrier to crossing the junction. When the system is in equilibrium ($V_{sd} = 0$), the energetic barrier for left moving holes, Φ_L , will be the same as the energetic barrier for right moving holes, Φ_R . Specifically, $\Phi_L = \Phi_R = \Phi_0$. Depending on the temperature, a certain fraction of these holes will have sufficiently high energy to overcome the barrier, leading to left (I_L) right (I_R) moving hole currents. There will be a corresponding electron current moving in the opposite direction that will add to this current, but have the same dependence on V_{sd} as the hole current. This baseline rate of charge transfer across the barrier defines the diode 'leakage' current, I_0 . Therefore, in equilibrium, $I_L = I_R = I_0$.



Figure 1.9 The effect of an applied V_{sd} on the band diagrams of the pn junction and Schottky junction. The source-drain bias is applied to the left hand side while the right hand side is grounded. The energies in band diagrams refer to the energies of electrons and therefore a positive V_{sd} corresponds to a lowering of the Fermi level. Application of a bias changes the effective energy barrier Φ - V_{sd} of the right moving holes and changes the right moving hole current. The magnitude of the hole currents are represented by the thicknesses of the lines.

The detailed expression for I_0 depends on the transport mechanism across the barrier, which is different for pn and Schottky junctions. However, in both cases, the population of thermallyexcited holes with enough energy to overcome the barrier is determined by the Fermi-Dirac distribution. Assuming that $\Phi_0 \gg k_B T$ and that there are no defects in the material that can trap the holes, we can write

$$I_0 = C(T) \exp\left(\frac{\Phi_0}{k_{\rm B}T}\right) \tag{1.2}$$

The factor C(T) may depend on temperature if the holes traverse the junction by thermionic emission as opposed to diffusion. Upon application of a source-drain voltage, the Φ_R will increase or decrease to $\Phi_R = \Phi_0 - eV_{sd}$, and the corresponding current will become,

$$I_{\rm R} = C(T) \exp\left(-\frac{\Phi_0 - eV_{\rm sd}}{k_{\rm B}T}\right) = I_0 \exp\left(\frac{eV_{\rm sd}}{k_{\rm B}T}\right) . \tag{1.3}$$

On the other hand, Φ_L will not change with bias and therefore the left moving current does not vary with bias:

$$I_{\rm L} = -I_0.$$
 (1.4)

The total current will then be $I_{sd} = I_R + I_L$

$$I_{\rm sd} = I_0 \left[\exp\left(\frac{eV_{\rm sd}}{k_{\rm B}T}\right) - 1 \right]. \tag{1.5}$$

This is the ideal diode equation. Equations 1.2-1.5 are plotted in Figure 1.10. When a reverse bias ($V_{sd} < 0$) is applied, the barrier for right moving holes is increased and I_R is 'shut off'. With increasing reverse bias, I_{sd} approaches a constant value, $-I_0$. For a forward bias ($V_{sd} > 0$), I_R exponentially increases. For a sufficiently large forward bias ($eV_{sd} \gg k_BT$) the exponential term in Equation 1.5 is dominant and $I_{sd} \cong I_0 \exp\left(\frac{eV_{sd}}{k_BT}\right)$. In this regime, the logarithm of I_{sd} is linearly proportional to V_{sd} (Figure 1.10c).



Figure 1.10 Plotting the ideal diode equation. a) Plots of a) I_L and I_R (Equation 1.3 and Equation 1.4) with respect to source-drain bias. $I_0 = 1$ nA. B) The ideal diode equation (Equation 1.5) which is achieved by adding I_L and I_R . C) A log plot of the ideal diode equation.

Qualitatively the pn junction and Schottky barrier have similar behavior. However, important quantitative distinctions arrive when considering the mechanism by which carriers traverse the barrier. In a pn junction, the flow of current is an injection of minority carriers, which must diffuse away from the junction. The current is therefore limited by the diffusion of minority carriers, which occurs through recombination with majority carriers (Figure 1.11a). In Schottky diodes, assuming the intrinsic region is shorter than the carrier diffusion length, current flows through thermionic emission instead of through diffusion. Carriers injected into the metal recombine essentially instantaneously and there is no need for minority carriers diffuse away like in the pn junction (Figure 1.11b).



Figure 1.11 Mechanisms of diode transport in an a) pn junction and b) Schottky diode. c) Experimentally measured I_{sd} - V_{sd} characteristics for commercial pn (1N914A, purple) and Schottky (SD101, orange) diodes.

In a pn junction in which the semiconductor has defects, recombination can occur through defect states within the bandgap. This mechanism of recombination is most often described by the Shockley-Read-Hall (SRH) model, which alters the diode equation with the introduction an ideality factor, n,³³

$$I_{\rm pn} = I_0 \left[\exp\left(\frac{eV_{\rm sd}}{nk_{\rm B}T}\right) - 1 \right]. \tag{1.6}$$

Depending on the energy of the defect states within the bandgap, *n* can range from 1 to 2 in the SRH model. n > 1 reduces the slope of $I_{sd}(V_{sd})$ in the exponential region. In the suspended CNT system, the lack of defects leads to a pn junction current I_{pn} with ideality factor near unity (Section 3.5.6).

In a Schottky diode, the current is not limited by recombination, and therefore n = 1. In addition, the velocity of carriers that cross the barrier is an important parameter and the velocity changes with temperature.³⁴ This dependence on the velocity of the carriers increases the relative importance of carriers with high kinetic energy and the thermionic emission current is more sensitive to temperature than the diffusion current. Specifically, I_0 becomes temperature dependent (see Equation 1.2). Both currents however, are still dominated by the exponential term as Equation 1.5 implies.

The particular temperature dependence of I_0 for a Schottky diode is dependent on the dimensionality of the system. For a one-dimensional system like a CNT, $I_0 = A_c A_r T$, where A_c is the contact area and A_r is the 1D Richardson constant.^{35,36} With these considerations we arrive at I_{sd} (V_{sd}) for 1-D Schottky diodes,

$$I_{\rm SB,1D} = A_{\rm c}A_{\rm r}T\left[\exp\left(\frac{eV_{\rm sd}}{k_{\rm B}T}\right) - 1\right]$$
(1.7)

Figure 1.11c shows I_{sd} (V_{sd}) data from commercial pn junction (1N4150) and Schottky (SD101) diodes. The ideality factors of the diodes can be determined from the slope of the exponential turn-on. The fitted ideality factors are n = 1.06 for the Schottky diode and n = 1.96 for the pn junction diode, consistent with the above discussion. Is not surprising that the transport is dominated by trap-assisted recombination in the pn junction diode because these are low quality, inexpensive diodes bought in bulk for hobbyist projects. The presence of traps does not affect the current in a Schottky diode, because the current is not limited by recombination.

The Schottky diode barrier height will depend on the work function alignment of the metal and CNT. A wide range of barrier height is possible, $0 < \Phi_0 < E_g$. If the barrier height becomes sufficiently small ($\Phi_0 < k_B T$), the current is no longer limited by thermionic emission and the contact will be Ohmic, obeying Ohms law instead.

Another important property of both pn and Schottky diodes is that under reverse bias the intrinsic region length will lengthen. This can be understood with a parallel plate capacitor model where the two plates of the capacitor are the p-type and n-type semiconductor. In the case of a bulk semiconductor pn junction, the plates correspond to the space charge regions in the intrinsic region itself.³³ In the case of the CNT pn junction the plates correspond to the doped sections of

the CNT. The electric field in the capacitor is related to the doping level of the semiconductors, and the voltage across the capacitor is equivalent to the source-drain bias. The relationship between reverse bias and intrinsic region length is explored in more detail in Section 5.6.

1.3.3 Optical response of pn junctions

The pn junction is the fundamental building block for optoelectronic applications. Optoelectronic devices include devices that convert light into electrical currents or voltages, and devices that convert electrical currents into light. When a photon is absorbed in a semiconductor, it will create an electron-hole pair. In an isolated semiconductor, there is no reason for the electron or hole to move in any particular direction (i.e. no asymmetry) and they will eventually recombine. However, the electric field of the pn junction introduces the necessary asymmetry to split apart the photogenerated electron-hole pairs. In general, this system is called a photodiode, represented by the circuit element in (Figure 1.12a). In the absence of a source-drain bias, the device converts light into electrical energy. Such a device is the basis of solar cell technology. In a well-designed conventional photodiode, the photogenerated current will just add to the 'dark' diode current (Equation 1.5) and the $I_{sd}-V_{sd}$ characteristic will be shifted downward. Figure 1.12b show a plot of Equation 1.5 with and without the presence of a photogenerated current. The parameters that went into generating these curves are typical of a commercial silicon solar cell.



Figure 1.12 Schematic of the working principle of a photodiode. The separation of a photogenerated electron-hole pair by the electric field present in the pn junction intrinsic region.
b) Theoretical *I*_{sd}-*V*_{sd} curves for a silicon solar cell with (red) and without (black) illumination.

To make pn junctions in CNTs, we fabricate the CNT split-gate devices (Figure 1.6). The motivation for building these devices is to measure and optimize the PCQY (Equation 1.1) of photocurrent generation in CNT pn junctions (Section 1.2.3).

1.3.4 Scanning photocurrent microscopy

To study the optoelectronic properties of the CNT pn junction and measure the PCQY (Equation 1.1), we utilize scanning photocurrent microscopy (SPCM). The details of the SPCM are given in Appendix 8 but here we give a brief overview.

The main function of the SPCM is to position a focused laser spot on the device at an arbitrary position on the surface of a nanoscale device. The position of the focused laser spot is raster scanned to form a map of the local photocurrent response of the device. Figure 1.13a shows a schematic of the SPCM operating on a CNT split-gate device. Figure 1.13b shows the photocurrent resulting from the CNT when it is doped into a pn junction is overlaid on top of a schematic of the device. When the laser spot is positioned over the pn junction in the center of

the CNT, a photocurrent is measured. In this picture, we see a photocurrent profile in the shape of the laser beam profile. This results because photocurrent only comes from the intrinsic region (see Section 5.2), which is much shorter than the beam waist.



Figure 1.13 Schematic of the scanning photocurrent microscope. a) Schematic of the SPCM operating on a CNT split-gate device. b) Photocurrent image projected over a schematic of the device that is doped into a pn junction. Dividing the number of electrons collected by photons absorbed results in a PCQY = 40% for this image.

Our goal with this image is to extract the PCQY (Section 1.2.3). This is accomplished by determining, within a given amount of time, the number of electrons extracted from the device and dividing by the number of photons absorbed. The number of electrons extracted is immediately determined from the measured photocurrent. Determining the number of photons absorbed, on the other hand, is a much greater challenge as will be discussed along with the other details of the PCQY measurement method in Chapter 5.

Using the method outlined in Chapter 5, the PCQY result for the photocurrent image in Figure 1.13b is 40%. This is an order of magnitude larger than previously observed in the literature for

similar devices.³⁷ This improved PCQY was achieved in part through a more in-depth understanding of the device physics as explained in Chapter 5.

1.4 Summary

We have discussed new physics that may arise due to strong e-e interactions. In semiconductors without e-e interactions, the electronic and optical properties are described by the same bandgap $E_g = E_{opt}$. In Section 1.2.2 we outlined how the situation is different in a system with strong e-e interactions and $E_g \neq E_{opt}$. The optical gap relates to optical phenomena where a simultaneous electron and hole are created. The transport gap describes the transport of one type of charge carrier. Strong e-e interactions also affect the relaxation pathways of photogenerated carriers. In Section 1.2.3 we discussed the process carrier multiplication, where multiple electron-hole pairs can be created from the same photon, and how it could potentially lead to highly efficient photovoltaics. Finally, in Section 1.2.4 we introduced the concept that surrounding the CNT in a dielectric environment will reintroduce dielectric screening and reduce the strength of the e-e interactions.

To measure the phenomena associated with strong e-e interactions in CNTs we have used suspended CNT split-gate devices. This introduction reviews the semiconductor devices physics that is required to understand the behavior of these devices. We began with semiconductor interfaces in Section 1.3.1, which are fundamental to understanding a semiconductor device. In particular, we examined the electrostatics of pn and metal-semiconductor junctions, both of which are present when the device is operated as a diode or photodiode. We are often interested in the response when an electrical bias is applied between the source and drain electrodes of our devices, and in Section 1.3.2 we review the effect of a source-drain bias on pn and metal-

semiconductor junctions. Finally, we review the optoelectronic response of pn junction (Section 1.3.3) and show example data from a CNT pn junction.

Looking forward, In Chapter 2 we will give an overview of the theoretical electronic and optoelectronic properties of CNTs in the zone-folding approximation. In the zone-folding approximation, the band structure of CNTs is derived from the non-interacting tight binding band structure of graphene with an additional boundary condition of continuity of the CNT wave function around the CNT axis. The optical spectra of CNTs is highly dependent on the particular way a CNT is rolled up from a graphene sheet, and we will be able to understand this dependence within the zone-folding approximation. We finally discuss the spectrally-dependent absorption cross section of CNTs and understand its structure in terms of the f-sum rule.

In Chapter 3 we investigate the electronic transport in the suspended CNT split-gate devices. We understand the two basic modes of operations of the device, the field-effect transistor and diode. Understanding the electronic transport when the device is doped into a pn junction (diode) is particularly important because that is also how we operate the device as a photodiode to study the optoelectronic properties of CNTs. In this chapter, we investigate the source-drain current versus source-drain voltage when the device is doped into a pn junction (I_{sd} - V_{sd} characteristic). By measuring the I_{sd} - V_{sd} characteristic varying the metal contact work function and temperature we develop a detailed model for the I_{sd} - V_{sd} characteristic. Our model helps explain variations in the I_{sd} - V_{sd} characteristic observed for similar devices in the literature.

In Chapter 4, we use the understanding of the electronic transport in the split-gate devices to probe the effects of strong e-e interactions on the electronic properties of CNTs. We measure how the electronic transport is affected by immersing a CNT in a dielectric environment. We are able to observe the large sensitivity of the transport gap on dielectric environment in CNTs. In Chapter 5, we explore the optoelectronic properties of the CNT split-gate devices. Using the understanding of the device physics developed in Chapter 3, we are able to isolate the photo response of the pn junction and overcoming the detrimental effect of the Schottky barriers on the optoelectronic response. Then we develop a method of extracting the PCQY from the SPCM data and measure a PCQY of approximately 30%, which is an order of magnitude larger than previously observed in the literature. We observe signatures of carrier multiplication in the photon energy dependence of the PCQY. Finally, in Chapter 6, we explore opportunities to increase the PCQY above 100%.

CHAPTER 2

Electronic and optical properties of CNTs

2.1 Introduction

In this section, we will describe a theoretical framework to understand the electronic and optical properties of CNTs. First, the electronic band structure of CNTs is derived in the zone-folding model. The band structure is important for understanding the electronic transport behavior of CNT devices (Section 3.4.1). The band structure is also needed to understand the optical properties of CNTs. The optical transition energies are sensitive to the physical structure of the CNT, and we will be able understand this dependence in terms of the zone-folding approximation. Finally, the strong e-e interactions present in CNTs affect the spectrally-dependent absorption and we discuss the empirical formula for the absorption cross section.

2.2 Tight binding band structure (Zone-folding model)

A carbon nanotube can be described as a graphene sheet rolled up into a cylinder. Our starting point for describing the optoelectronic characteristics will then be to examine the band structure of graphene. The real space lattice of graphene is a hexagonal structure described by the lattice vectors $\vec{a_1}$ and $\vec{a_2}$, shown in Figure 2.1a. The corresponding reciprocal lattice vectors, $\vec{b_1}$ and $\vec{b_2}$ lead to the reciprocal lattice shown in Figure 2.1b. The first Brillouin zone is another (rotated) hexagon. The corners of the hexagon are described by six high-symmetry points in k-space. There are two unique high-symmetry points labeled K and K'. The vectors pointing to K and K' are given by,

$$\vec{K} = \frac{(\vec{b_1} - \vec{b_2})}{3} \qquad \vec{K'} = \frac{(\vec{b_2} - \vec{b_1})}{3}.$$
(2.1)

The other 4 corners of the hexagon are equivalent to \vec{K} and $\vec{K'}$ because they can be related to \vec{K} and $\vec{K'}$ by the addition of a reciprocal lattice vector.

In the hexagonal structure of graphene each carbon atom has three bonding partners. Three of carbon's four valence electrons sp₂ hybridize to form strong covalent bonds to these neighbors.³⁸

The fourth electron resides in the out-of-plane p_z orbital, which is half filled in undoped graphene. These p_z orbitals form the conduction band for electrons in graphene. The electronic structure can be derived by considering a tight-binding model with these p_z orbitals which results in the dispersion relation.³⁹

$$E(k_{\rm x}, k_{\rm y}) = \pm \gamma_1 \sqrt{1 + 4\cos(\frac{\sqrt{3}ak_{\rm y}}{2})\cos\left(\frac{ak_{\rm x}}{2}\right) + 4\cos^2\frac{ak_{\rm x}}{2}}$$
(2.2)



Figure 2.1: The band structure of graphene. a) The real space lattice of graphene. The lattice vectors are defined by $\vec{a_1} = \sqrt{3}a_0\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$ and $\vec{a_2} = \sqrt{3}a_0\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$ b) The reciprocal lattice. The outer hexagon outlines the reciprocal lattice points and the inner hexagon is the first Brillouin zone. c) The graphene tight-binding band structure (Equation 2.2). d) Close up of the band structure around one of the K points.

A plot of Equation 2.2 is shown in Figure 2.1c. The band structure is of particular interest near the K points and a zoom in around one of the K points is shown in Figure 2.1d. The first thing to

notice is that the valence and conduction bands meet, but do not overlap. In fact, the density of states is exactly zero only at the K points.⁴⁰ Therefore, graphene is classified as a semimetal.

The other notable aspect of the band structure around the K points is the linear relationship between *E* and $\vec{k'} - \vec{K}$, which gives rise to a conical band structure near the Dirac point, often referred to as the Dirac cone. The dispersion relation can be quantified by defining a wave vector $\vec{k} = \vec{k'} - \vec{K}$, where $\vec{k'}$ points from the center of the Brillouin zone, and \vec{K} refers to either \vec{K} or $\vec{K'}$ as defined in Equation 2.1 (Figure 2.2c). Therefore \vec{k} is a vector that points from a given Dirac point (Figure 2.2c). For small $|\vec{k}|$ Equation 2.2 reduces to

$$E(\vec{k}) = \hbar v_F |\vec{k}|. \tag{2.3}$$

The linear dispersion relation implies zero effective mass, and the carriers move at an effective speed of light called the Fermi velocity $v_F = 10^6$ m/s. The carriers in this region have been named Dirac fermions.

When rolling up a CNT there is an additional boundary condition on the wave function that it must be periodic around the CNT circumference. In the zone-folding approximation, we assume that the band structure of CNTs is simply determined from the graphene band structure (Figure 2.1c) with this additional boundary condition. The following discussion borrows heavily from reference ⁴¹. The boundary condition (Born–von Kármán boundary condition) can be represented as

$$\vec{C} \cdot \vec{k'} = 2\pi j, \tag{2.4}$$

where $\vec{C} = n \, \vec{a_1} + m \vec{a_2}$ is the chiral vector (Figure 2.2a) and *j* is an integer. This equation defines the set of allowed $\vec{k'}$ vectors in the graphene reciprocal space. The allowed $\vec{k'}$ vectors point to a series of lines, one for each *j*, that are perpendicular to \vec{C} . These lines are called cutting lines and are shown in the Brillouin zone in Figure 2.2b.



Figure 2.2 Schematic of CNT cutting lines. a) The real space lattice of graphene and definition of the chiral vector. In this case (n,m) = (5,1). b) Cutting lines in reciprocal space of graphene. C) Zoom-in around the K point.

The electronic structure of CNTs is then a set of one-dimensional subbands, indexed by *j*, which are cross-sections of the graphene band structure along the cutting lines. The lowest energy subbands will arise from the cutting lines that pass nearest to the Dirac points. The subbands near K and K' are degenerate, so it is sufficient to consider the subbands near the K point, as depicted in Figure 2.2c.

We are interested in the dispersion relation of the j^{th} subband, $E_j(k_{\parallel})$, where k_{\parallel} is the wave vector along the axis of the CNT (Figure 2.2c). In the Dirac approximation we assume that the j^{th} subband is close enough to the Dirac points that Equation 2.3 still holds and $E_j(k_{\parallel})$ will be

$$E_j(k_{\parallel}) = \hbar v_f \sqrt{k_{\perp,j}^2 + k_{\parallel}^2}$$
(2.5)

 $k_{\perp,j}$ will be a constant depending on *j* (Figure 2.2c), which can be determined by considering that $\vec{k}_{\perp,j}$ will be parallel to \vec{C} . The total wavevector $\vec{k'}$ can then be written as

$$\vec{k'} = \vec{K} + \vec{k_{\parallel}} + \left| \vec{k_{\perp,J}} \right| \hat{C}$$
(2.6)

Which must obey the boundary condition Equation 2.4. Plugging Equation 2.6 in to Equation 2.4 and solving for $|k_{\perp,j}|$ gives

$$\left|k_{\perp,j}\right| = \frac{2\pi j - \vec{K} \cdot \vec{C}}{|C|} \tag{2.7}$$

The dot product $\vec{K} \cdot \vec{C}$ is calculated using the definition of \vec{K} (Equation 2.1), the definition of the chiral vector $\vec{C} = n\vec{a_1} + m\vec{a_2}$, and the orthogonality relation $\vec{a_i} \cdot \vec{b_j} = 2\pi\delta_{ij}$. Combining these equations gives the result,

$$\left|k_{\perp,j}\right| = \frac{2p}{3d},\tag{2.8}$$

where d is the diameter of the CNT and we have defined the integer

$$p = |3j \pm (n - m)|. \tag{2.9}$$

The integer p represents the distance of a cutting line away from the Dirac point in units of $\frac{2}{3d}$ (see Equation 2.8). The possible values of p depend on the chirality of the CNT. If mod(n-m,3) = 0, then p = 0 is possible. This means that there exists a *j* such that $|k_{\perp,j}| = 0$ and a cutting line that passes through the Dirac point exists. Therefore, CNTs with this kind of chirality will not have a bandgap and are metallic. Electron-electron effects actually reintroduce a bandgap in metallic CNTs, as we discuss in Chapter 4. For CNTs with mod(n-m,3) = 1 or 2, the cutting lines will miss the Dirac point and the CNT will be semiconducting. Table 2.1 summaries the possible values of p for both categories of CNTs.

Туре	mod(<i>n</i> - <i>m</i> ,3)	р
Metallic	0	0,3,6,9
Semiconducting	1 or 2	1,2,4,5,7,8

Table 2.1: The possible values of p for metallic (mod(n-m,3) = 0) and semiconducting (mod(n-m,3) = 1, 2) CNTs.

We can calculate the dispersion relation $E_j(k_{\parallel})$ by plugging $|k_{\perp,j}|$ into Equation 2.5.

$$E_j(k_{\parallel}) = \hbar v_F \sqrt{\left(\frac{2p}{3d}\right)^2 + k_{\parallel}^2}$$
(2.10)

Figure 2.3 shows the dispersion relation and corresponding density of states (DOS) of metallic and semiconducting CNTs.



Figure 2.3 Band structure (left) of and DOS (right) of semiconducting (top) and metallic (bottom) CNTs.

2.3 Optical transitions

We now discuss the optical transitions for CNTs. In the non-interacting zone-folding model described so far, the optical transitions would be simply determined by calculating the joint

density of states from the DOS presented in Figure 2.3.⁴² Because of the symmetry of the valence and conduction bands, the shape of the absorption spectrum would look identical to the DOS. Specifically, the optical absorption would be a series of sharply peaked optical transitions with tails on the high-energy side. However, in section 1.2.2 we discussed how the optical properties of the CNT are strongly affected by e-e interactions. The electron and hole created during an optical excitation become bound into an exciton. This dramatically affects the line shape for each optical transition from the zone-folding prediction. Specifically, the excitonic transitions are still a series of peaks, one for each subband, but are described by a Lorentzian line shape. We discuss the spectrally-dependent absorption in detail Section 2.4, but first we seek to understand the structure of the energies of the excitonic transitions, i.e. the photon energies corresponding to the peak of the Lorentzian line shape.

The optical transition energies, in contrast to the transition line shape, are not dramatically affected by electron-electron (e-e) interactions. This was explained in Section 1.2.2 in terms of the near cancelation of the self-energy and exciton binding energy. This weak dependence of the excitonic transition energies on the e-e interactions strength implies that the structure of the excitonic optical transition energies can be qualitatively understood within the framework of the zone folding picture. In fact, photoluminescence spectroscopy was one of the first optical measurement techniques applied to CNTs and were first analyzed in terms of the zone folding approximation. However, the observed ratio of the first and second optical transition energies was experimentally found to be $\frac{E_{22}}{E_{11}} = 1.75$, instead of the zone folding approximation prediction, $\frac{E_{22}}{E_{11}} = 2$. This discrepancy was known as the ratio problem. Theory had predicted that e-e interactions could explain the discrepancy.⁴³ In 2005 Wang et al. showed experimentally that the

optical transitions in CNTs arise from excitons, confirming the central role of e-e interactions in determining the optical transitions of CNTs.¹⁸

We will see that the structure of the excitonic resonance energies can be qualitatively understood in terms of the zone-folding picture, but a quantitative relationship between chiral index and excitonic resonance energies is critical for much of the work in this thesis. In particular, such a relation allows for the determination of the chiral index of a CNT from peaks measured in the spectrally-dependent photocurrent (Section 5.5). The chiral index is directly related to the diameter of the CNT through the equation $d = \frac{a_{c-c}}{\pi \sqrt{(n^2 + n*m + m^2)}}$, where a_{c-c} is the carbon-carbon bond length. Determining the chiral index also allows for a calculation of the spectrally-dependent absorption cross section (Section 2.4), and the absorption cross section is a critical component in the calculation of the photocurrent quantum yield of CNT pn junctions (Chapter 5). Finally, the subband index, which denotes which subbands carriers are being excited between, can be determined for an observed excitonic resonance if the chiral index is known. The subband index of the subband index for an optical transition is important for considering carrier relaxation dynamics, particularly carrier multiplication.⁴⁴

In 2012 Liu et al. measured resonance energies of 206 CNTs suspended in air with Rayleigh scattering spectroscopy and directly measured the chirality with TEM afterward.⁴⁵ The large sample size allowed for the development of an empirical formula to predict the set of resonances for every possible chiral index. Here we will first provide a brief overview of the empirical formula and develop an intuition for structure-property relationships such as the dependence of the resonance energies on CNT diameter and chiral angle. In the next section we will describe how once the chiral index is identified, the spectrally-dependent absorption cross section can be calculated, by using another work from Liu et al.

The empirical formula for the resonance energies is cast in terms of a renormalized zone folding approximation. The effect of electron-electron interactions manifests itself as a 'renormalization' of the Fermi velocity. The p^{th} excitonic resonance energy is described in terms of the wavevectors pointing to the lowest energy state of the p^{th} subband. Because $\vec{k}_{\parallel,p} = 0$ for these states, $\vec{k}_{\perp,p}$ as defined in Equation 2.8 is the relevant wavevector.

$$E_p(\vec{k}_{\perp,p}) = 2\hbar v_{F,p} k_{\perp,p} + \beta k_{\perp,p} \log \frac{3k_{\perp,p}}{2} + k_{\perp,p}^2 [\eta_p + \gamma_p \cos 3\theta] \cos 3\theta$$
(2.11)

In this equation, $v_{F,p}$ is a renormalized Fermi velocity, β is a fit parameter describing deviation from the Dirac approximation at larger wavevectors and renormalization effects. η_p and γ_p describe the effect of a finite CNT diameter, which causes a curvature of the graphene surface and affects the band structure. The curvature effect depends on the polar angle θ which is the angle of $\vec{k}_{\perp,p}$ measured from \vec{a}_1 as defined in Figure 2.1. θ is equivalent to the CNT chiral angle $\alpha = \tan^{-1}\left(\frac{\sqrt{3}m}{2n+m}\right)$ within π radians, depending on whether $\vec{k}_{\perp,p}$ points upward or downward in k-space.⁴⁶ γ_p is an extra phenomenological parameter important in accurately predicting the resonance energies for small chiral angles. The values of the coefficients are outlined in Reference 46.

The average ratio of $\frac{E_{22}}{E_{11}}$ produced by this equation is 1.75, resolving the ratio problem discussed earlier. The electron-electron interactions that cause $\frac{E_{22}}{E_{11}} \neq 2$ are contained the β term and the *p* dependent Fermi velocity, $v_{F,p}$. When $\beta = 0$ the ratio increases to 1.92, and further if v_F does not depend on *p*, the ratio is equal to 2. $v_{F,p}$ and β therefore contain interesting information about the electron-electron interactions, which is discussed in detail in Ref. 45.

Figure 2.4 plots the resonance energies as a function of diameter predicted by Equation 2.11 for a variety of chiralities. The red and blue colors represent positive and negative contributions

of the curvature term. The reproduced data from the empirical formula agrees with experiment within 15 meV.⁴⁶ The general structure Figure 2.4 can be qualitatively understood in terms of the zone folding approximation. The resonance energies are more closely spaced for larger diameters and have an approximately $\frac{1}{a}$ dependence, consistent with the $\frac{1}{a}$ dependence of the cutting line spacing. At higher energies, the $\frac{1}{a}$ dependence is less accurate, because the cutting lines are now crossing in a region of the graphene band structure where the Dirac approximation (Equation 2.3) does not apply. There is a larger spread in the transition energies for smaller diameter CNTs because the separation of Dirac point and any cutting lines will be more sensitive to the particular chiral angle. The resonances for semiconducting CNTs come in pairs, which correspond to the pairs of cutting lines on each side of the Dirac point. For metallic CNTs the resonances fit in between the spaces of the semiconducting resonance pairs.



Figure 2.4 Optical transition energies of a) semiconducting and b) metallic CNTs. The optical transistors are calculated from Equation 1.10. The q value indicated by the symbol and the color represents the sign of the curvature term.

We now discuss the origin of the curvature term in Equation 2.11 and its effect on the structure of the resonance energies. In a CNT with finite curvature, the tight-binding matrix elements will be different perpendicular and parallel to the axis of the CNT, causing a distortion of the graphene band structure. Yang et al. showed that, in the case of axial strain, the Dirac point moves $(\Delta \vec{D})$ at an angle 3α measured clockwise with respect to \vec{C} , where α is the CNT chiral angle.⁴⁷ Curvature leads to a shift that is opposite to that of strain (coupling decreases along circumference instead of axis) so the relevant angle is $3\alpha + \pi$ (Figure 2.5a).



Figure 2.5 The effect of curvature on a-b) semiconducting and c) metallic CNTs.

The shift of the Dirac point will change the magnitude of k_{\perp} for each optical resonance. The magnitude of the change will be $|\Delta k_{\perp}| \propto |\vec{C} \cdot \Delta \vec{D}| \propto \cos 3\alpha$ (Figure 2.5a). The change in the wavevector for the p^{th} transition, $\Delta k_{\perp,p}$, will be positive or negative depending on whether $\vec{k}_{\perp,p}$ is parallel or antiparallel to \vec{C} , respectively. For example, for CNTs with mod(n-m,3) = 1, $\vec{k}_{\perp,1}$ is antiparallel to \vec{C} and therefore $\vec{k}_{\perp,1}$ will decrease and the resonance will shift downward (Figure 2.5a), and vice versa for CNTs with mod(n-m,3) = 2 (Figure 2.5b). For each sequentially higher resonance, $\vec{k}_{\perp,p}$ will flip direction, and the energy shift will change sign. For metallic CNTs in the absence of curvature, each optical transition arises from two degenerate cutting lines that pass on both sides of the Dirac point. With curvature effects, the shift in the Dirac point will

cause a positive Δk_{\perp} for one cutting line and negative Δk_{\perp} for the other, and each optical transition splits into two closely spaced peaks (Figure 2.5c).

The above discussion is neatly contained within the $\cos(3\theta)$ dependence of the curvature term in equation 2.11.⁴⁵ The polar angle θ_i of $\vec{k}_{\perp,i}$, is equivalent to α within π radians and $\cos(3\theta) = \pm \cos(3\alpha)$ contains the sign of the shift. The subscript *i* is not the same as *p* and refers to the subscript in S₁₁, S₂₂, M₁₁, etc. as outlined in Figure 2.4. For semiconducting CNTs, $\theta_i = \alpha + i * \pi$ when $\operatorname{mod}(n-m,3) = 1$ and $\theta_i = \alpha + (i+1) * \pi$ when $\operatorname{mod}(n-m,3) = 2$. For metallic CNTs, $\theta = \alpha$ for the higher energy peak and $\theta = \alpha + \pi$ for the lower energy peak.

2.4 Absorption cross section

2.4.1 Empirical formula

Even though the excitonic transition energies have a resemblance to the single particle picture, the frequency-dependent absorption cross section per carbon atom, $\sigma_C(\hbar\omega)$, will be altered dramatically by e-e interactions. Determination of $\sigma_C(\hbar\omega)$ is critical for calculations of the photocurrent quantum yield (Chapter 5).

Measuring $\sigma_c(\hbar\omega)$ of individual CNTs has historically been difficult, but recently has been accomplished.⁴⁸ Systematic determination of $\sigma_c(\hbar\omega)$ for CNTs of many different chiralities has revealed accurate rules for predicting $\sigma_c(\hbar\omega)$ for a given chiral index.⁴⁹ $\sigma_c(\hbar\omega)$ is calculated by adding together the individual contributions from each optical transition $\sigma_{c,p}(\hbar\omega)$, where *p* is the subband index (see Table 2.1). The contribution from the *p*th optical transition, with energy *E*_p, is given by

$$\sigma_{C,p}(E) = \frac{\Sigma_p}{\pi} \cdot \frac{w_p}{\left(E - E_p\right)^2 + w_p^2} + \frac{\Sigma_p}{\pi a} \cdot conv \left(\frac{b \cdot w_p}{\left(E - E_p\right)^2 + \left(b \cdot w_p\right)^2}, \frac{\Theta[E - (E_p + \Delta)]}{\sqrt{E - (E_p + \Delta)}} \right)$$
(2.12)

The first term represents the excitonic transition and is described by a Lorentzian peak centered at E_p with linewidth w_p and oscillator strength Σ_p . The second term represents the band-to-band transition and is described by the convolution of a broadened Lorentzian with the 1-D density of states. The constants a, b, and Δ represent the relative oscillator strength, broadening, and the energy offset of the continuum transition. The relative strength of the continuum transition is determined by $a \approx 5$. w_p , Σ_p , a, b, and Δ are all determined from empirically verified expressions.⁴⁹ Plotted below are the absorption cross sections calculated for three different chiralities.



Figure 2.6: $\sigma_c(\hbar\omega)$ calculated for semiconducting CNTs of three different diameters. The average absorption cross section is shown as a dashed line.

2.4.2 <u>F-Sum rule</u>

The structure of $\sigma_c(\hbar\omega)$ can be understood in the context of a partial f-sum rule. f-sum rules are ubiquitous in many fields of physics. Generally, in the context of optical interactions, the frequency-integrated absorption cross section, $\int d\omega \sigma(\hbar\omega)$, will only depend on the number of electrons that participate in optical transitions in the integrated frequency range,⁵⁰ given that that the integration range is sufficiently large to encompass all optical transitions exhibited by those electrons. We refer to $\int d\omega \sigma(\hbar\omega)$ as the spectral weight.

An insightful demonstration of the f-sum rule is to consider the absorption cross section an electron when modeled as a damped simple harmonic oscillator, $\sigma_{SHO}(\omega)$. $\sigma_{SHO}(\omega)$ can be calculated to be in the form of a lorentzian,⁵⁰

$$\sigma_{\rm SHO}(\omega) = \gamma \frac{\pi e^2}{2\epsilon_0 mc} \frac{1}{(\omega_0 - \omega)^2 + \frac{\gamma^2}{4}}$$

where ω_0 and γ are the resonant frequency and damping coefficient of the oscillator, respectively. Integrating σ_{SHO} over frequency gives the result

$$\int \sigma_{\rm SHO} \, d\omega = \frac{\pi e^2}{2\epsilon_0 mc} \approx \frac{10^{-16} {\rm cm}^2}{{\rm atom}} {\rm eV}$$

A value that only depends on fundamental constants, and not ω_0 or γ . Therefore,

 $\int \sigma_{\text{SHO}} d\omega$ itself is a universal constant and is in fact used to define the "oscillator strength" of an atomic transition. The oscillator strength is a number describing how many effective classical oscillators are participating in an atomic transition.⁵⁰

Because graphene and CNTs have one optically active electron per atom, we should be able to roughly estimate the average absorption cross section of graphene. This estimate is motivated by the quantum-classical correspondence principle. Assuming the absorption resulting from optical transitions between p_z orbitals extends over the range of ~10 eV,⁵¹ $\sigma_{C,avg} \approx 10^{-17} \frac{\text{cm}^2}{\text{atom}}$. Indeed, this is remarkably to the experimental average cross section of graphene and CNTs of $\sigma_{C,avg} \approx$

$$7 \cdot 10^{-18} \frac{\mathrm{cm}^2}{\mathrm{atom}}$$

Elegant demonstrations of the f-sum rule have been performed by electrostatically doping graphene and observing a spectral weight transfer from interband to intraband transitions.^{52,53} As the Fermi level is raised, some optical transitions become Pauli blocked. Counter-balancing this effect, the rising carrier density increases the low frequency Drude response of the material. The changes in integrated absorption for both frequency regions was demonstrated to be exactly equal and of opposite sign.

The f-sum rule also applies to spectral weight transfer caused by quantum confinement effects. Graphene has a spectrally flat absorption cross section, $\sigma_{C,gr} \approx 6 \cdot 10^{-18} \text{ cm}^2/\text{eV}$, which can be derived by applying Fermi's golden rule to the Dirac dispersion relation (Equation 2.3).^{54,55} Quantum confinement in a CNT causes the graphene absorption cross section to become condensed into excitonic peaks. Looking at Figure 2.6, at an exciton resonance, the CNT absorption cross section per carbon atom can reach many times $\sigma_{C,gr}$, but off resonance, σ_C is less than $\sigma_{C,gr}$. Integrating $\sigma_C(\hbar\omega)$ over an interval that includes several exciton peaks yields a value approaching the integrated absorption cross-section of graphene, as expected from the f-sum rule.⁵⁶

The f-sum rule also predicts that $\int d\omega \sigma_c(\hbar\omega)$ should be invariant with respect to the degree of confinement, which is related to the diameter of the CNT. The diameter invariant integrated $\sigma_c(\hbar\omega)$ was observed in the devices measured by Liu et al, within the error expected to arise from the finite energy measurement window.⁴⁹ This consequence of the f-sum rule allows us to reason through the diameter dependence of other aspects of $\sigma_C(\hbar\omega)$. For example, the energy peak spacing in the zone-folding approximation scales as $\frac{1}{d}$, and therefore to maintain a constant integrated spectral weight, the spectral weight of the p^{th} peak Σ_p (see Equation 2.12) must scale as $\frac{1}{d}$. Indeed, the empirical formula⁵⁶ for Σ_p includes this $\frac{1}{d}$ dependence:

$$\Sigma_p = \frac{45.9}{(p+7.5)d} \, 10^{-4} \, \mathrm{nm}^2 \, \mathrm{eV}. \tag{2.13}$$

A spectral weight per peak inversely proportional to the diameter has also been calculated by applying Fermi's golden rule to the CNT excitonic wave functions.⁵⁷

The $\frac{1}{d}$ dependence of Σ_p can be used to predict a universal value for the spectral weight per peak per unit length $\Sigma_L = \Sigma_p N_L$ Here, $N_L = \frac{4\pi d}{\sqrt{3}\alpha^2}$ is the number of atoms per unit length, and α is the graphene lattice constant 0.249 nm.³⁷ Combining N_L with Equation 2.13 we achieve,

$$\Sigma_{\rm L} = \frac{0.537}{(p+7.5)} \,\mathrm{nm} \,\mathrm{eV}.$$
 (2.14)

Because $N_{\rm L}$ scales linearly with d, $\Sigma_{\rm L}$ is independent of the diameter. $\Sigma_{\rm L}$ is the area under an excitonic peak when plotting the absorption cross section per length, $\sigma_L(\hbar\omega)$., The width of the excitonic peaks, $w_{\rm p}$, experimentally increases with photon energy with dependence $w_{\rm p} = 0.0194 \ \hbar\omega$.⁵⁶ Therefore, the peak absorption cross section per unit length, $\sigma_{L,peak}(\hbar\omega)$, will be inversely proportional to the photon energy. We can quantify this result by considering the expression for $\sigma_L(\hbar\omega) = N_{\rm L} \sigma_C(\hbar\omega)$ (Equation 2.12) and assuming the absorption is dominated by the excitonic term,

$$\sigma_{\text{L,peak}}(\hbar\omega) = \frac{8.8}{(7.5+p)\hbar\omega} \text{ nm eV.}$$
(2.15)

For typical CNT diameters and our experimental photon energy range, the index p varies from p = 1 to approximately p = 5. Therefore, the denominator does not vary dramatically and we can make the approximation that p = 1,

$$\sigma_{\rm L,peak}(\hbar\omega) \approx \frac{1}{\hbar\omega} \,\mathrm{nm}\,\mathrm{eV}\,,$$
 (2.16)

In Figure 2.7 both $\sigma_c(\hbar\omega)$ and $\sigma_L(\hbar\omega)$ are plotted for three different CNTs. For a given photon energy $\sigma_{c,peak}(\hbar\omega)$ varies with the diameter of the CNT, but $\sigma_{L,peak}(\hbar\omega)$ does not. Regardless of the chiral index, $\sigma_{L,peak}(\hbar\omega)$ follows the curve of Equation 2.16, which is plotted as a dashed line along with $\sigma_L(\hbar\omega)$ in Figure 2.7b. This result, that $\sigma_{L,peak}$ is simply a function of $\hbar\omega$, is useful experimentally. A precise chiral identification is not required to estimate the optical absorption properties, provided that the optical excitation is tuned to an excitonic resonance energy.



Figure 2.7: Comparing $\sigma_C(\hbar\omega)$ and $\sigma_L(\hbar\omega)$ a) Absorption cross section per carbon atom for the three CNTs in Figure 1.11. b) The Absorption cross section per unit length for the same three CNTs.

Despite the approximation p = 1, the dashed line in Equation 2.16 fits the peak heights very well, even at large p. The background absorption from arising the lower energy continuum transitions (second term in Equation 2.12) contributes to the peak height at higher p. This background absorption 'lifts' the high p-value excitonic peaks back up to follow the curve of Equation 2.16.

CHAPTER 3

Electronic devices built from suspended carbon nanotubes and split gate electrodes

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3.1 Introduction

The experimental system through which we study the interesting electronic and optoelectronic properties of CNTs is the suspended CNT split-gate device. Such devices can be configured as transistors or diodes with a variety of electronic characteristics. In this chapter we develop an understanding of the electronic transport through these devices. We will understand the characteristics of their two basic modes of electrical operation, the CNT field-effect transistor (CNTFET) and the CNT diode. In the CNTFET mode, both gate electrodes are operated with the same voltage, uniformly doping the CNT.

To use the device as a diode, opposite voltages are applied to the gates, which dopes the CNT into a pn junction. The diode characteristics are of particular interest for two reasons. First, doping the CNT into a pn junction is how we operate the device as a photodiode and study the optoelectronic characteristics, which is the main motivation for fabricating these devices (Chapter 5). Understanding the behavior of the device in the absence of light (diode mode) will give us helpful insight to understanding the behavior of the illuminated device (photodiode mode). Second, many other research groups have fabricated suspended split-gate devices, with a significant amount of variability in the reported diode behavior. The main result of this chapter is the development of a model for our diode behavior that also can explain the variations observed in the literature.

3.2 Device fabrication

Figure 3.1a and Figure 3.1b show SEM images of a CNT split-gate device. A CNT is grown across a trench to connect source and drain electrodes. Suspending the CNT removes the complicating factor of electrostatic disorder contained in the SiO₂ substrate (Section 4.2). At the



Figure 3.1 Suspended CNT split-gate devices. a,b) SEM images and c) schematic of the suspended CNT split-gate devices d) AFM cross section of the trench.

The devices were fabricated starting with 4-inch Si/SiO₂ wafers (500 nm oxide layer) on which gate electrodes were patterned and deposited (W/Pt 5 nm/60 nm). A layer of SiO₂ (800 nm thickness) was used to bury the gates. The source and drain electrodes were then patterned and deposited (W/Pt 5 nm/60 nm). Reactive ion etching was used to dig a 770 nm trench between the source and drain electrodes. The Pt electrodes define the edge of the trench. CNT growth catalyst (1 nm Ti / 20 nm SiO₂ / 1 nm Fe) was deposited on top of the source and drain electrodes. CNTs were grown using chemical vapor deposition in a tube furnace at 800 °C. By having growth as the last step we create pristine suspended CNTs free of chemical residue. The chips were shuttled in to avoid electrode degradation. The growth recipe consists of a 1 minute 1 SLM H₂ anneal

followed by a 5 minute growth phase with 0.15 SLM ethanol, 0.3 SLM methanol, and 0.45 SLM H₂. The ethanol and methanol are introduced into Ar gas with a bubbler.

3.3 Electrostatics

The equilibrium band diagrams (Section 1.3.1) of the CNT split-gate device in the two basic gating configurations are shown in Figure 3.2. Applying the same voltage (V_g) to both gates simultaneously (Figure 3.2a,b) uniformly dopes the CNT and operates the device as a CNT field effect transistor (CNTFET). Alternatively, applying voltages of opposite magnitude ($V_{g,1} = -V_{g,2}$) dopes the CNT into a pn junction (Figure 3.2c) and operates the device as a diode.

The CNT is capacitively coupled to the gate electrodes, and charge accumulates on the CNT from the application of the gate voltages (Section 3.4.2). Because the Fermi level is constant throughout the system, this electrostatic doping corresponds to a raising (n-doping) or lowering (p-doping) of the conduction and valence band edges. In other words, the chemical potential of electrons (the Fermi level) does not vary along the axis of the CNT, but the energies of the quantum states themselves, which are affected by the electrostatic potential, vary along the axis of the CNT. The ability to electrostatically dope the CNT is a unique feature of nanoscale materials, because changing the doping level of a bulk semiconductor requires chemical doping. In our system, the doping level can be changed in a continuous and reversible way.



Figure 3.2 Band diagrams for the basic configurations of the CNT split-gate device. a,b) Fieldeffect transistor and c) pn junction. The gray shading indicates intrinsic regions.

The behavior of the device is not only dependent on the doping of the CNT, but also the nature of the metal electrode/CNT interfaces. The electrodes represent boundary conditions on the electrostatic potential and the positions of the conduction and valence bands at the metal surface are fixed with respect to the metal Fermi level. If the metal Fermi level aligns within the CNT bandgap, Schottky barriers form at the metal CNT interfaces (see Section 1.3.1). These Schottky barriers are represented by the gray shaded regions in Figure 3.2, which represent intrinsic regions (regions where the Fermi level is within the bandgap). An intrinsic region also forms between the p-doped and n-doped CNT in the pn junction configuration (Figure 3.2c)

3.4 CNTFET

3.4.1 Transistor curve

To characterize the devices after growth they are first operated as CNTFETs. In this measurement the conductivity, $G = I_{sd}/V_{sd}$, is measured as a function of a common gate voltage (V_g) that is applied to both gate electrodes. V_{sd} is the voltage between the source and drain electrodes and I_{sd} is the resulting source-drain current. Usually, $V_{sd} = 25$ mV and V_g is swept from -10 V to 10 V, continuously changing the electrostatic band profile from that of Figure 3.2a to Figure 3.2b. $G(V_g)$ for a Semiconducting CNT (mod(n - m, 3) = 1 or 2, see Section 2.2) is


the CNTFET is in the 'off state'.

Figure 3.3 CNTFET $G(V_g)$ for a a) semiconducting and b) narrow-gap CNT

 $G(V_g)$ for semiconducting CNTs can be understood in terms of the Schottky barriers that form at the metal-CNT interfaces (Section 1.3.1).³¹ In the case of platinum metal electrodes in an ambient environment, the metal work function is sufficiently large that the Fermi level will align near the CNT valence band edge. Therefore, only small Schottky barriers will form when the CNT is p-doped (negative V_g), and holes will easily transfer in and out of the CNT. This is in contrast to the n-doping the CNT (positive V_g) where the formation of large Schottky barriers impede the flow of current.

Figure 3.3 shows $G(V_g)$ for a 'metallic' CNT (mod(n - m, 3) = 0, see Section 2.2). The gate voltage modulates the conductance, implying the presence of a bandgap. This is contradictory to the zone-folding picture presented in Section 2.2 which predicts that CNTs with mod(n - m, 3) = 0 have no bandgap. This small bandgap arises in part form e-e interactions and is discussed in more detail in Chapter 4. To avoid confusion, we refer to CNTs with mod(n - m, 3) = 0 as

'narrow-gap' CNTs. Narrow-gap CNTs have bandgaps on the order of 100 meV and therefore thermionic emission over or tunneling through the Schottky barriers will be possible for both pdoping and n-doping and no 'off-state' exists.

On each chip there are 48 devices and after a typical growth process a CNT will traverse/grow across the trench in approximately 1/5 of these devices. In practice, chips are probed with $V_g = -2$ V to ensure that semiconducting CNTs are in a conductive state and will be detected. A nonzero conductance indicates the presence of one or more CNTs connecting the electrodes. After postselection for CNTs with good electrical conductivity, we have counted 110 narrow-gap CNTs and 187 wide-gap CNTs over the last 3 years of experiments. Assuming the chirality produced during our growth process is random, this result is in approximate agreement with the prediction of the zone folding model that the ratio of semiconducting to metallic CNTs should be 2:1 (Section 2.2). The ratio is actually 1.7:1, which can be explained by semiconducting CNTs with low conductivity (larger bandgap) that were not detected with the typical probing preamp sensitivity. Hysteresis effects could also cause a semiconducting CNT to stay in the off state.

3.4.2 <u>Coulomb blockade spectroscopy</u>

The CNT split-gate devices can be operated as single-electron transistors by cooling to sufficiently low temperature and using the device in CNTFET mode. At low enough temperature the energy required to put an electron onto the CNT, the charging energy, is much larger than $k_{\rm B}T$. In this regime, it is possible to study the energetics of CNTs individual quantum states by scanning $V_{\rm g}$ and $V_{\rm sd}$. This kind of measurement is called Coulomb blockade spectroscopy. Amazing insight into the fundamental physics of electrons in CNTs has been achieved by performing Coulomb blockade spectroscopy.⁵⁸ In this section, we provide a brief overview use

Coulomb blockade spectroscopy and how it is used in this thesis. For a general reference on quantum dot Coulomb blockade measurements the reader is referred to reference 59.

Figure 3.4 illustrates a Coulomb blockade spectroscopy measurement. The Figure 3.4a-d show schematic representations of the quantum states in the CNT, source electrode, and drain electrode. The CNTs quantum states (black lines) are separated in energy by a combination of a capacitive charging energy and quantum level spacing. The gate voltage raises or lowers the electrostatic potential in the CNT and the states move up or down in energy. In the energy diagrams of the source and drain contacts, the filled quantum states below the Fermi Level are shaded black. Applying a source-drain bias raises the Fermi level of the left electrode with respect right electrode. The CNT is coupled to the source and drain electrodes, and current will flow if there is a quantum state in between the source and drain electrode Fermi levels. Figure 3.4e shows a schematic of the resulting current that through the CNT as a function of gate and source-drain voltage, $I_{sd}(V_g, V_{sd})$. The (V_g, V_{sd}) coordinates corresponding to the Figure 3.4a-d are labeled a-d.



Figure 3.4 Analyzing low-temperature measurements of $I_{sd}(V_g, V_{sd})$. a-d) The energy level diagrams illustrate the alignment of electron energy levels in the source electrode, the CNT and the drain electrode. e) Schematic representation of $I_{sd}(V_g, V_{sd})$. Blue represents positive current, red represents negative current, white represent no current. The $(V_{\rm g}, V_{\rm sd})$ coordinates corresponding to the energy diagrams a-d are marked on the plot.

Figure 3.4a shows the energy diagram for an applied gate voltage such that the first electron state in the conduction band aligns with the metal Fermi levels when $V_{sd} = 0$. In this case, an electron state is accessible and current can flow even for small V_{sd} . Increasing the gate voltage slightly, the states will be shifted in energy and the device will no longer conduct. However, as Figure 3.4b shows, the quantum state can again be accessed by applying a larger V_{sd} , and the device becomes conducting again. Considering the energy diagrams for the continuum of gate voltages and the necessary V_{sd} that would have to be applied to access a quantum state, a diamond shape of zero current will form in the $I_{sd}(V_g, V_{sd})$ plot, which is called a Coulomb diamond. Figure 3.4c shows how a similar situation arises for the first hole in the valence band.

We use Coulomb blockade spectroscopy in this thesis as a tool to measure the transport gap of narrow-gap CNTs (Section 4.4). To find the transport bandgap, E_g , we look for the (V_g , V_{sd}) coordinates at the peak of the largest diamond (point d). The first electron state and the first hole state span the eV_{sd} energy window and we have $E_g = V_{sd}/e$. We often make use of the straight edges of the Coulomb diamonds. If the maximum V_{sd} in the measurement range is less than E_g/e , point d can be found by extrapolating the edges of the diamond. The gate coupling to the first hole state is sometimes different than the gate coupling to first electron state. In such cases, the opposite edges of the diamond are not parallel.

Figure 3.4 shows Coulomb blockade spectroscopy data for one of our devices. Figure 3.4a shows $I_{sd}(V_g, V_{sd})$ which indeed has the same structure as Figure 3.4e. By extrapolating the black lines we can determine the location of point d and determine E_g . For comparison, the room temperature $G(V_g)$ is shown in Figure 3.4b. It is easier to see the Coulomb diamonds by plotting the differential conductance dI_{sd}/dV_{sd} . dI_{sd}/dV_{sd} for hole and electron doping are shown in Figure 3.4c and Figure 3.4d, respectively. The extra lines within the conducting regions arise from excited quantum states.⁵⁸



Figure 3.5 Transport measurements of a CNT device to determine $E_g = 71.8 \pm 6.2$ meV. This device is slightly different than the CNT split-gate devices described in Section 3.2 and the source-drain electrode separation is L = 700 nm. a) $I_{sd} (V_{sd}, V_g)$ at T = 2 K. b) $G(V_g)$ at 300K c) $dI_{sd}/dV_{sd} (V_{sd}, V_g)$ at T = 2 K on the p-type side. d) $dI_{sd}/dV_{sd} (V_{sd}, V_g)$ at T = 2 K on the n-type side.

It is possible to determine the gate capacitance and total capacitance from Coulomb blockade spectroscopy. Figure 3.6 shows the Coulomb diamonds for n-doping of another device.⁵⁹ The width of the Coulomb diamonds depends on the gate capacitance, C_g , the total capacitance, C, and the energy level spacing ΔE :

$$\Delta V_{\rm g}(N \rightarrow N+1) = \frac{e}{C_{\rm g}} + \left(\frac{C}{C_{\rm g}}\right) \frac{\Delta E}{e} \; .$$

From Figure 3.6 we find $\Delta V_g(N \rightarrow N+1) = 22 \text{ mV}$. For a 2 µm-long CNT, $\Delta E < 1 \text{ meV}$. We conclude that $C_g \sim 7$ aF.



Figure 3.6 Coulomb blockade measurements at 30 mK. Labels show the number of holes occupying the dot. The height of the blockade diamonds is 9 mV. The width of the diamonds is 22 mV.

The gate capacitance can be used to estimate the charge density per unit length, λ , for different gating configurations. For example, if $|V_g|=10$ V, then

$$|\lambda| = \frac{7 \text{ aF}}{2 \ \mu \text{m}} (10 \text{ V}) = 220 \ \frac{e}{\mu \text{m}} ,$$

where *e* is the elemental charge. If the device is operated as a pn junction, the split-gate voltages are equal and opposite ($V_{g1} = -V_{g2}$). The left gate has some coupling to the right side of the CNT and vice versa. Therefore, $|\lambda|$ will be slightly less when the device is operated in the pn junction configuration.

3.5 CNT pn junction

3.5.1 Introduction

The pn junction is a crucial building block for modern electronics and optoelectronics. To create and study pn junctions in new nanomaterials, many researchers have turned to dual-gated lateral devices. Lateral pn junctions in WSe₂^{60,61}, MoSe⁶², and carbon nanotubes (CNTs)^{2,63} have

been used to investigate the potential of those nanomaterials for applications such as solar cells, photodetectors and LEDs.

Measurements of pn junctions in nanomaterials are often complicated by the metalsemiconductor junctions in series with the pn junction. Previous work on nanomaterial-based field-effect transistors has shown that the Schottky barriers associated with metal-semiconductor junctions drastically affect device properties.^{35,64,65} However, the effect of Schottky barriers on nanomaterial-based diodes is relatively unexplored. For example, CNT diode devices have been reported with a diversity of device characteristics that cannot be accounted for by a simple pn junction.^{66,67} In this work, we elucidate the role of Schottky barriers in lateral pn junction devices made from nanomaterials. We vary the Schottky barrier heights (SBHs) and establish the effect of Schottky diode contacts on the overall properties of a CNT pn junction device.

We have chosen suspended CNTs with dual gates as our model system (Figure 3.1).^{63,67–69} This system is an ideal prototype for nanomaterial-based diodes for several reasons. First, the fully-suspended CNT is a "clean" system. There are no complications associated with substrate-induced disorder, doping, or screening. Second, we can characterize the diameter and chirality of the CNT under study,⁶³ allowing precise comparison between device characteristics and electronic structure. Third, our device geometry creates Schottky barriers that are sufficiently long (> 100 nm) so that transport past the barrier is via thermionic emission, rather than a complicated mixture of tunneling and thermionic emission.^{35,64} Lastly, the SBH is tunable. The work function (WF) of the metal contacts changes gradually when the device is transferred from laboratory air to a vacuum environment. Previous authors have used this affect to study the role of SBH on CNT field-effect transistors (CNTFETs),^{31,70} and here we use the effect for the first time to study the role of SBH on a nanomaterial-based diode.

3.5.2 pn junction I_{sd} - V_{sd} characteristics

Figure 3.7a shows the I_{sd} - V_{sd} characteristic of one of our suspended CNT split-gate device at various (V_{g1} , V_{g2}). The measurements are taken in a vacuum environment. In contrast to the behavior of a conventional pn junction diode (Section 1.3.2), we observe two regimes where the current exponentially increases and two regimes where the current plateaus. The first exponential increase begins near $V_{sd} = 0$ V. As V_{sd} is increased, the current level eventually reaches a plateau. Then, a second exponential increase is observed starting at a voltage, V_{shift} . V_{shift} depends on the magnitude of the applied gate voltages. Finally, there is a second exponential increase, and the current reaches a second plateau.

Figure 3.7b-d show I_{sd} - V_{sd} characteristic from devices with similar suspended geometry measured by other authors. Even though the devices have very similar design, the I_{sd} - V_{sd} characteristics show significant variations. Like us, Liu et al. (Figure 3.7b) saw a current plateau before an exponential increase with tunable V_{shift} . Liu et al. mention the first current plateau but do not explain its origin, and did not report a second plateau. In contrast to our measurements, and Liu's measurements, Chang et al. and Barkelid et al only saw an exponential turn-on occurring at $V_{sd} = 0$ V and no plateaus. Chang et al. (Figure 3.7c) observed that the first exponential increase in current was independent of the magnitude of the gate voltages. They modeled their linear current roll-off (not shown in Figure 3.7c) with a Schottky diode in parallel with a tunnel resistance. Barkelid et al. (Figure 3.7d) also saw a linear roll-off, and modeled it with a series contact resistance.



Figure 3.7 I_{sd} - V_{sd} characteristics of suspended split-gate devices. a) I_{sd} - V_{sd} characteristics of our suspended CNT split-gate devices (Device 1) and b-d) other suspended CNT split-gate devices in the literature.^{66,67,69} The numbers in parts a and b represent the voltages applied to the split-gates V_{g1} and V_{g2} .

The characteristics of CNTFETs are known to be sensitive to changes in the metal work function (WF) caused by the presence or absence of chemical adsorbates on the surface of the metal electrodes (Section 1.3.1).^{31,70} Changing the metal WF alters the positioning of the metal Fermi level with respect to the conduction and valence band edges, and therefore affects the height of the Schottky barriers formed at the metal-CNT contacts. Specifically, the CNTFET conductivity, $G(V_g)$, exhibit a small Schottky barrier for holes in an ambient environment and small Schottky barrier for electrons in a vacuum environment. The known sensitivity of CNTFET device characteristics to the metal WF led us to hypothesize that the observed variation in I_{sd} - V_{sd} characteristics (Figure 3.7) might be related to variations in the metal WF.

To test this hypothesis we measured the $G(V_g)$ and I_{sd} - V_{sd} characteristics while the device was left in a vacuum environment for two weeks (Figure 3.8). Leaving the device in vacuum (at room temperature) causes a gradual change in the metal WF as surface adsorbates are slowly removed. Consistent with the previous literature, the p-type conductivity of the CNTFET decreases and the n-type conductivity increases (Figure 3.8a). The n-type and p-type conductivities are related to the electron Schottky barrier height, Φ_e , and the hole Schottky barrier height, Φ_h , respectively (Figure 3.8, inset). These observations imply a decrease in Φ_e and increase in Φ_h , consistent with a decrease in metal WF. Because the bandgap is equal to the sum of the Schottky barrier heights, $E_g = \Phi_h + \Phi_e$, the decrease in Φ_e is expected to balance the increase in Φ_h .



Figure 3.8 Comparison of the CNTFET characteristics and the CNT diode characteristics of Device 2.a) CNTFET conductivity measured at $V_{sd} = 25 \text{ mV}$. b) CNT diode characteristics measured at $V_{g1} = V_{g2} = -5 \text{ V}$. The color of the curves changes from black to green to orange as the device is left in vacuum for two weeks. All measurements are taken at T = 295 °K.

Figure 3.8b shows the diode characteristics of the same device measured over the same period of time. When the device is in an ambient environment (black curve), the current is below the noise floor of our measurement for $V_{sd} < 0.8$ V. For $V_{sd} > 0.8$ V, The current increases exponentially before finally reaching a linear roll-off. After the device is put in a vacuum environment for approximately one day, the double plateau behavior develops. As the device sits in vacuum over the course of two weeks, the current of the first plateau increases in magnitude while the current of the second plateau decreases in magnitude.

3.5.3 Equivalent circuit model

Comparing Figure 3.8a to Figure 3.8b we note that the CNTFET conductivity at $V_g = -4$ V is well correlated to the second plateau in the diode current. Similarly the CNTFET conductivity at $V_g = +4$ V is well correlated to the first plateau in the diode current. This correlation implies that the first plateau is related to Φ_e and the second plateau is related to Φ_h . We postulate that the current of the first plateau is proportional to rate at which electrons can be emitted over the ntype Schottky barrier, which is equivalent to the reverse bias current of the n-type Schottky diode, $I_{0,SBe}(\Phi_e)$. The Second plateau is proportional to rate at which holes can be emitted over the p-type Schottky barrier, which is equivalent to the reverse bias current of the p-type Schottky diode, $I_{0,SBh}(\Phi_e)$.

We have developed an equivalent circuit model (Figure 3.9a) that contains these relationships and explains the I_{sd} - V_{sd} characteristic for arbitrary metal WF. The circuit consists of a pn junction diode in the center of the CNT, and two Schottky diodes at the metal-CNT interfaces. When the pn junction is forward biased, both Schottky diodes are reverse biased. The low-resistance doped regions of the CNT are represented as wires. Transport in the doped regions is likely ballistic because the room temperature majority carrier scattering length is approximately 1µm in suspended CNTs.⁷¹ In our model, the current plateaus correspond to the saturation currents of the Schottky diodes (Figure 3.9d, regions labeled R2 and R4). The pn junction determines the current before the first plateau and in between the plateaus (Figure 3.9d, regions labeled R1 and R3). We now formalize this model and quantify the key parameters for the device shown in Figure 3.8b (Device 1).



Figure 3.9 Understanding the I_{sd} - V_{sd} characteristic. a) Equivalent circuit for the suspended CNT pn junction. b,c) Schematic band diagrams along the axis of the CNT for the regimes R2 and R4 as labeled in part d. d) I_{sd} - V_{sd} characteristic of Device 1 after the device is left in vacuum for two weeks. The I_{sd} - V_{sd} characteristic is divided into four regimes labeled R1 –R4, as described in the text.

The source-drain bias is distributed across three circuit elements such that

$$V_{\rm sd} = V_{\rm SBh} + V_{\rm pn} + V_{\rm SBe} , \qquad (3.1)$$

where V_{SBh} , V_{SBe} , and V_{pn} correspond to the voltage drop across the p-type Schottky barrier, the n-type Schottky barrier, and the pn junction. In each transport regime, a different circuit element is 'limiting' the current and changes in V_{sd} are associated with changes in the voltage drop across that particular element. This current limiting behavior arises because the three circuit elements are in series,

$$I_{\rm sd}(V_{\rm sd}) = I_{\rm SBh}(V_{\rm SBh}) = I_{\rm pn}(V_{\rm pn}) = I_{\rm SBe}(V_{\rm SBe}), \qquad (3.2)$$

where I_{SBh} , I_{SBe} , and I_{pn} are the currents flowing through the p-type Schottky barrier, n-type Schottky barrier, and pn junction, respectively. Thus, I_{sd} is constrained by the coupled equations (see Section 1.3.2):

$$I_{\rm SBh} = I_{0,\rm SBh} \left(1 - e^{\frac{-eV_{\rm SBh}}{k_{\rm B}T}} \right)$$
(3.3)

$$I_{\rm pn} = I_{0,\rm pn} \left(e^{\frac{eV_{pn}}{nk_{\rm B}T}} - 1 \right)$$
(3.4)

$$I_{\rm SBe} = \begin{cases} I_{0,\rm SBe} \left(1 - e^{-\frac{eV_{\rm SBe}}{k_{\rm B}T}} \right), V_{\rm SBe} < V_{\rm shift} \\ G_0(V_{\rm SBe} - V_{\rm shift}), V_{\rm SBe} > V_{\rm shift} \end{cases}$$
(3.5a,b)

where $I_{0,SBh}$, $I_{0,pn}$, and $I_{0,SBe}$ are the saturation currents of the respective diodes, G_0 is the conductance quantum, V_{shift} is the width of R2 and *n* is the ideality factor of the pn junction. Equations 3.3 and 3.5a are flipped in sign compared to a conventional Schottky diode due to the reversed orientation. The piecewise function (eq. 3.5) describes an unusual voltage dependence of I_{SBe} . A mechanism for this voltage-triggered change was proposed by Liu et al. and is discussed further below.⁶⁷

To complete our model, we consider the factors influencing the saturation currents $I_{0,SBh}$, $I_{0,pn}$, and $I_{0,SBe}$. Using a 1-D Landauer formalism for electron transport in a CNT, Bosnik et al. calcuated⁷²

$$I_{0,pn} = \frac{8ek_{\rm B}}{h} \tau_{\rm pn} \ T e^{-\frac{E_{\rm g}}{k_{\rm B}T}},\tag{3.6}$$

where τ_{pn} is the transmission coefficient over the pn junction and E_g is the bandgap of the CNT at the location of the pn junction ($E_g >> k_BT$). Applying the same approach to a 1-D Schottky contact yields

$$I_{0,SBh} = \frac{4ek_B}{h} \tau_h T e^{-\frac{\Phi_h}{k_B T}}$$
(3.7)

$$I_{0,SBe} = \frac{4ek_B}{h} \tau_e T e^{-\frac{\Phi_e}{k_B T}},$$
(3.8)

where Φ_h and Φ_e are the Schottky barrier heights for holes and electrons, and τ_h and τ_h are the transmission coefficients across the two Schottky barriers. Equations (3.7) and (3.8) are consistent with the 1D Richardson constant formalism previously used to analyze CNT 1D contacts.^{35,36}

It is instructive to qualitatively describe the features of our equivalent circuit model. Figure 3.9d shows a typical I_{sd} - V_{sd} characteristic for (Device 1 on Day 14 of vacuum environment). The four distinct regimes of $I_{sd}(V_{sd})$ are labeled in Figure 3.9d as R1, R2, R3 and R4. The following discussion is summarized in Table 3.1.

Regime 1 (R1, Figure 3.9d):

To determine the behavior at small V_{sd} , consider the zero-bias conductance, which has the same form for each circuit element,

$$\frac{dI}{dV_{\rm sd}}\Big|_{V_{\rm sd}=0} = \frac{e}{k_{\rm B}T}I_0.$$

The reverse bias leakage currents, I_0 , for each element are given by Equations 3.6-3.8. If the Fermi level is within the bandgap, like in the situation of Figure 3.9d, $\Phi_e \approx \Phi_e \approx \frac{E_g}{2}$. Therefore, the circuit element with the largest zero-bias conductance is the pn junction. V_{sd} will mostly drop across the pn junction and the current will be determined by $I_{pn}(V_{pn})$. The mechanism of charge transport in R1 corresponds to a conventional pn junction: minority carrier injection of holes from the p-type region into the n-type region and vice versa.³³ The holes will recombine with electrons after diffusing the minority carrier diffusion length, L_d (Figure 3.9b). **Regime 2** (**R2**, Figure 3.9d): When $I_{pn}(V_{pn})$ approaches $I_{0,SBe}$, V_{pn} cannot grow any larger because of the condition $I_{pn} = I_{SBe}$. Instead, additional applied V_{sd} will drop as a reverse bias across the n-type Schottky barrier (V_{SBe}) and the current will plateau at $I_{0,SBe}$. The current is limited by the rate at which majority carriers (electrons) can traverse the reverse-biased n-type Schottky barrier ($I_{0,SBe}$, see Figure 3.9a).

Regime 3 (R3, Figure 3.9d): Reverse biasing of the n-type Schottky barrier will increase the length the barrier, and cause a corresponding decrease in L_n . When $V_{sd} > V_{shift}$, L_n is sufficiently short that minority carriers (holes) can traverse the n-type region and reach the right-side electrode (Figure 3.9b). This condition is met when $L_n < L_d$. In this regime, $V_{pn} = V_{sd} - V_{shift}$, where V_{shift} is the voltage width of R2. V_{shift} corresponds to the voltage drop across the n-type Schottky barrier that was required to make $L_n = L_d$. This effect was first described by Liu et al.⁶⁷ and is included in our model with the piecewise equation 3.5.

Regime 4 (**R4**, Figure 3.9d): $I_{pn}(V_{pn})$ will eventually approach $I_{0,SBh}$. At this point, V_{pn} cannot grow any larger, because of the condition $I_{pn} = I_{SBh}$. Further increase of V_{sd} will be distributed to the p-type Schottky barrier (V_{SBh}) and the current will plateau at $I_{0,SBh}$.

Regime	Condition	Limiting circuit element
R1	$I_{\rm sd} < I_{0,\rm SBe}$	pn junction
R2	$I_{\rm sd} = I_{0,\rm SBe}$	n-type Schottky diode
R3	$I_{0,\mathrm{SBe}} < I_{\mathrm{sd}} < I_{0,\mathrm{SBh}}$	pn junction
R4	$I_{\rm sd} = I_{0,\rm SBh}$	p-type Schottky diode

Table 3.1 Conditions and the limiting circuit element for each of the regimes (R1-R4) described in Figure 3.9.

The value of V_{shift} is strongly modulated by the gate voltages (Figure 3.7a). Liu et al. explain this phenomenon by considering the effect of V_{g1} and V_{g2} on the length L_n . Asymmetrically gating the device with a larger positive gate ($|V_{g2}| > |V_{g1}|$, Figure 3.7c) increases L_n . This results in a larger V_{shift} . We also find that increasing $|V_{g1}|$ and $|V_{g2}|$ symmetrically changes V_{shift} (Figure 3.7a). In general, a larger $|V_{g2}|$ causes a larger electric field within the n-type Schottky barrier, \mathcal{E}_{SBe} . Large \mathcal{E}_{SBe} makes L_n less sensitive to V_{sd} .

3.5.4 Temperature dependence

To further our transport model we measured temperature dependent diode curves. Based on the circuit model of Figure 3.9a, we expect the first and second plateaus in the I_{sd} - V_{sd} characteristic to correspond to $I_{0,SBe}$ and $I_{0,SBh}$, respectively. The temperature dependence of these plateaus will then be described by Equations 3.7-3.8.

Figure 3.10a shows the temperature dependence of the I_{sd} - V_{sd} characteristic of Device 2 after being left in vacuum. Both $I_{0,SBe}$ and $I_{0,SBh}$ decrease with decreasing temperature, consistent with Equations 3.7-3.8. We extract $I_{0,SBe}$ and $I_{0,SBh}$ by averaging over the plateaus. A Richardson plot, a plot of $\ln(\frac{I_{0,SBe}}{T})$ and $\ln(\frac{I_{0,SBh}}{T})$ vs 1/T, is shown in Figure 3.10b. A linear fit gives the Schottky barrier heights and transmission coefficients $\Phi_e = 192 \pm 14$ meV, $2.7 \times 10^{-3} < \tau_e < 1.1 \times 10^{-2}$, $\Phi_h = 219 \pm 24$ meV, and $0.4 < \tau_h < 3.9$.



Figure 3.10 Extracting the SBH height with temperature dependent I_{sd} - V_{sd} characteristics. a) Temperature dependent diode curves of Device 2. B) 1D Richardson plot of the first (red) and second (blue) current plateaus. The extracted Schottky barrier heights are $\Phi_e = 192 \pm 14 \text{ meV}$ and $\Phi_h = 219 \pm 24 \text{ meV}$.

In Figure 3.11 we use the transmission coefficients extracted above and the plateau currents of Figure 3.8b with Equations 3.7-3.8 to extract how the SBHs change over the course of two weeks in vacuum.



Figure 3.11. Φ_e, Φ_h , and $\Phi_e + \Phi_h$ extracted from the current plateaus of Figure 3.8.

 $\Phi_{\rm e}$ and $\Phi_{\rm h}$ are related by the equation $\Phi_{\rm e} + \Phi_{\rm h} = E_{\rm g}$, which gives a bandgap (near the metal contacts) $E_{\rm g} = 411 \pm 27$ meV. To compare this result with the optical bandgap, we measured the

spectrally-dependent photocurrent of this device which is shown Figure 3.12a.⁶³ By comparing the peak energies of the measured excitonic transitions to empirical formulas⁴⁵ (Section 2.3) we can determine the chirality of this CNT to be (n,m) = (29,10). The first excitonic transition for this chirality is $E_{11} = 430$ meV, approximately equal to the measured bandgap. This is an interesting result because, as discussed in Section 1.2.2, the electronic bandgap could be significantly larger than the first excitonic transition.¹⁴ Our observation that the electronic bandgap corresponds to the optical bandgap may be explained by screening from the nearby metal electrode.⁷³ This hypothesis is consistent with STM measurements, which have already provided experimental evidence of metal-induced reduction of CNT transport gaps.⁷⁴

In contrast to the electrostatically-screened environment near the metal electrodes, the pn junction is located in the center of the CNT, far from the metal electrodes. Previous experiments on CNT pn junctions,⁷⁵ scanning tunneling spectroscopy of CNTs,⁷⁴ and CNTs in dielectric environments,⁷³ suggest that E_g increases when screening is reduced. Therefore, we have considered the possibility that $E_g > \Phi_e + \Phi_h$. We achieve an excellent fit to our experimental data (See Section 3.5.5) by setting $\tau_{pn} = 1$ and $E_g = 500$ meV. A transmission coefficient of order unity is a reasonable assumption because the expected scattering length in the suspended CNT is greater than the pn junction intrinsic region length.⁷¹ We conclude that the I_{sd} - V_{sd} characteristics (Figure 3.8b) are consistent with a growing body of evidence for a screening-dependent transport gap in CNTs.



Figure 3.12 a) Spectrally-dependent photocurrent and b) calculated absorption cross-section for Device 2.The chirality and absorption cross section are determined following the procedure in Section 5.5.

3.5.5 Model curves

Figure 3.13 shows solutions to the coupled set of equations, Equations 1-4. The simulated device characteristics (Figure 3.13) are in excellent agreement with our measurements (Figure 3.8). To generate these curves, we make an array of exponentially spaced I_{sd} values and determine $V_{sd} = V_{SBh} + V_{pn} + V_{SBe}$ using the following equations,

$$V_{\rm SBh} = -\frac{k_B T}{e} \ln \left(1 - \frac{I_{\rm sd}}{I_{0,\rm SBh}} \right)$$
(3.9)

$$V_{\rm pn} = \begin{cases} \frac{k_B T}{e} \ln\left(\frac{I_{\rm sd}}{I_{0,\rm pn}} + 1\right), V_{\rm sd} < V_{\rm shift} \\ \frac{k_B T}{e} \ln\left(\frac{I_{\rm sd} - I_{0,\rm SBe}}{I_{0,\rm pn}} + 1\right), V_{\rm sd} > V_{\rm shift} \end{cases}$$
(3.10)

$$V_{\rm SBe} = \begin{cases} -\frac{k_B T}{e} \ln\left(1 - \frac{I_{\rm sd}}{I_{0,\rm SBe}}\right), V_{\rm sd} < V_{\rm shift} \\ V_{\rm shift}, V_{\rm sd} > V_{\rm shift} \end{cases}$$
(3.11)

The piecewise function for V_{pn} is a matter of book keeping (not a representation of a physical process). The synchronous change in Eqn. 3.10 and Eqn. 3.11 "resets" the voltage drop across

the pn junction and assigns all of V_{shift} to the Schottky barrier for electrons. This creates a smooth transition into the second exponential increase in current. In the calculation of $I_{0,\text{pn}}$, a bandgap $E_{\text{g}} = 1.2^*$ ($\Phi_{\text{e}} + \Phi_{\text{h}}$) is used. This increased bandgap in the center of the CNT is justified considering the screening of the Schottky barriers at the metal contacts (see Section 3.5.4)



Figure 3.13 Simulated I_{sd} - V_{sd} characteristic that closely match Figure 3.8. The SBH heights are varied from $\Phi_e = 250 \text{ meV}$ (dark green) to $\Phi_e = 170 \text{ meV}$ (orange), maintaining $\Phi_e + \Phi_h = 410 \text{ meV}$. Other free parameters are fixed: $\tau_h = 1$, $\tau_e = 5.5 \times 10^{-3}$, $\tau_{pn} = 1$, n = 1.3, $E_g = 500 \text{ meV}$ and $V_{shift} = 0.9 \text{ V}$.

Table 3.2 summarizes the parameters used to simulate the CNT device shown in Fig. 1e of the main text.

Table 3.2 Schottky barrier heights used to generate the model curves of Figure 3d of the main text. We constrain $\Phi_{\rm h} + \Phi_{\rm e} = 410 \text{ meV}$ and the other parameters that are common to all of the

Day	$\Phi_{\rm e}({\rm meV})$	$\Phi_{\rm h}({\rm meV})$
1	250	160
3	230	180
5	210	200
8	190	220
15	170	240

curves are $\tau_{pn} = 1$, n = 1.3, $\tau_e = 5.5 \times 10^{-3}$, $\tau_h = 1$, $V_{\text{shift}} = 0.9$ V, $E_g = 500$ meV.

3.5.6 <u>Ambient I_{sd}-V_{sd} characteristics</u>

Our discussion so far has focused on I_{sd} - V_{sd} characteristics in vacuum (day 1 – 15). We now comment on the I_{sd} - V_{sd} characteristics in an ambient environment, which are shown in Figure 3.14 and the black curve in Figure 3.8. In an ambient environment, the WF is sufficiently large to form Ohmic p-type contacts i.e. $\Phi_h \approx 0$ and $\Phi_e \approx E_g$. In this situation $I_{0,SBe}$ is below the noise floor of our measurement (showing that $\Phi_e > 320$ meV), and $I_{0,SBh}$ exceeds 200 nA (showing that $\Phi_h < 80$ meV). In addition, because the p-type contact is Ohmic, the current linearly increases beyond regime R3, instead of plateauing. This change in the I_{sd} - V_{sd} characteristic can be described by replacing the p-type Schottky diode of the equivalent circuit of Figure 3.9a with a series resistor. The I_{sd} - V_{sd} characteristic of a diode and resistor in series are described by the Wlambert function, $W(V_{sd})$.⁷⁶ Combining $W(V_{sd})$ with a V_{shift} gives an expression for the current:

$$I_{sd} = I_{0,pn} \left[\frac{nk_{\rm B}T}{I_{0,pn}R} W \left(\frac{I_{0,pn}R}{nk_{\rm B}T} e^{\frac{V_{\rm sd} - V_{\rm shift} + I_{0,pn}R}{nk_{\rm B}T}} \right) - 1 \right]$$
(3.12)

Fitting curves based on Equation 3.12 are shown in Figure 3.14. $I_{0,pn} = 300$ fA is chosen as the noise floor. $R \sim 1 \text{ M}\Omega$ is determined from the linear I_{sd} - V_{sd} regime ($I_{sd} > 1$ nA). The ideality factor, n, is close to unity for all I_{sd} - V_{sd} curves (1.2 < n < 1.3).



Figure 3.14 a) I_{sd} - V_{sd} characteristics for Device 3 in an ambient environment. Red dots correspond to symmetric n-type and p-type gating ($V_{g2} = -V_{g1} = 8$ V). Blue dots correspond to asymmetric gating ($V_{g2} = 4$ V, $V_{g1} = -8$ V). Equation 3.12 is used for curve fitting (black lines).

Fit lines have ideality factor n = 1.29 ($V_{g2} = -V_{g1} = 8$ V) and 1.25 ($V_{g2} = 4$ V, $V_{g1} = -8$ V). b) Device 4. Lightly gated to heavily gated. Orange, blue, green and red correspond to $V_{g2} = -V_{g1} = 2$, 4, 6, and 8 V respectively. Equation 3.12 is used for curve fitting (black lines). c) The ideality factors for the fitting curves in part b.

3.5.7 <u>FET mode $I_{sd}(V_{sd})$ </u>

We also took measurements of $I_{sd}(V_{sd})$ when the CNT was uniformly p-doped or n-doped (Figure 3.2a,b). In this situation, the device can be described with an equivalent circuit model of only two back-to-back Schottky diodes. Regardless of the sign of V_{sd} , one of the Schottky diodes will be reverse biased. Therefore, the current plateaus for both $V_{sd} < 0$ and $V_{sd} > 0$. Figure 3.15 shows the work function dependence of the FET $I_{sd}(V_{sd})$ measurement, which were taken at the same time as the measurements in Figure 3.8.



Figure 3.15: Work function dependence of the $I_{sd}(V_{sd})$ characteristics of Device 1 when the CNT is operated in FET mode. a) $I_{sd}(V_{sd})$ for n-doping ($V_{g1} = V_{g2} < 0$) and b) $I_{sd}(V_{sd})$ for p-doping ($V_{g1} = V_{g2} > 0$).

Figure 3.16 shows the temperature dependence of the FET $I_{sd}(V_{sd})$ measurement, which were taken at the same time as the measurements in Figure 3.10. Interestingly, the current plateaus in reverse and forward bias are not exactly equal, implying that the detailed nature of each individual CNT-metal contact is playing a role. Figure 3.16c shows a Richardson plot of the FET $I_{sd}(V_{sd})$ plateau currents alongside the plateaus of the diode $I_{sd}(V_{sd})$ (Figure 3.10) which show excellent agreement.



Figure 3.16. Temperature dependence of $I_{sd}(V_{sd})$ characteristics of Device 1 when the CNT is operated as a FET a) Temperature dependence for n-doping ($V_{g1} = V_{g2} < 0$) and b) Temperature dependence for p-doping ($V_{g1} = V_{g2} > 0$). c) Plateau currents for both FET mode (parts a and b) and diode mode (Figure 3.10b).

3.5.8 Discussion

Interestingly the Φ_{e} is slightly larger than Φ_{h} , even though $I_{0,SBe}$ is two orders of magnitude smaller than $I_{0,SBh}$. This discrepancy remains unexplained, but one factor that could contribute is a non-constant density of states of the platinum contacts around the Fermi level. Holes injected from the valence band will encounter a different density of states than electrons injected from the conduction band. Indeed, the density of states calculated for platinum is approximately 2-3 times larger near the valence band than the conduction band.⁷⁷ The transmission coefficient for carriers to travel between the metal contacts and CNT, which depends on the spatial overlap of the CNT and metal wave functions, may also be different at the two ends of the CNT, due to variability in the device fabrication process.

The proposed model can be used to explain variation in the I_{sd} - V_{sd} characteristics observed in the literature (Figure 3.7). The main discrepancy between measurements is the presence and magnitude of a first plateau in the current, $I_{0,SBe} \propto e^{\frac{-\Phi_e}{k_BT}}$. Liu et al. observed the I_{sd} - V_{sd} characteristic most similar to our devices. They observed the first plateau in current at a similar magnitude as our plateau. They do not show data above 5 nA, therefore, we cannot comment on the presence/absence of a second plateau. Barkelid et al. observed a linear current roll-off instead of a first plateau indicating an Ohmic n-type contact (i.e. a very small Φ_e). Chang et al. also observed a linear roll-off that they modeled with a Schottky diode in parallel with a tunnel resistance. However, this linear roll-off appears to be consistent with only a series resistance (Ohmic contact) for the doping regimes relevant for this study.

Differences in Φ_e could arise from different metal WFs and/or different bandgap CNTs. The differences in metal WF could arise from removal of surface adsorbates, differences in metal deposition method,¹¹ or simply using a different contact metal. Liu et al. used gold contacts instead of platinum. Gold has a smaller WF than platinum, consistent with the smaller Φ_e . Chang et al. and Barkelid et al. both mentioned that their measurements were taken in a vacuum environment. However, a shift in the metal WF is not sufficient to explain such large currents, because decreasing the metal WF would also increase Φ_h . Therefore, the devices used by Chang et al. and Barkelid et al. are likely utilizing smaller bandgap CNTs. An interesting possibility is that these studies are using narrow-gap CNTs, which we have observed can have bandgaps of approximately 200 meV (Chapter 4).

Temperature dependent measurements have been widely used in the literature to extract the SBH of nanoscale electronic field-effect transistors. A common method, used in both surface based (fabricated on SiO₂ surface) CNTFETs³⁵ and MoS₂ FETs⁶⁴, extracts the gate voltage dependent SBH, $\Phi(V_g)$, from the temperature dependence of the FET conductivity $G(V_g)$. The gate voltage where $\Phi(V_g)$ begins to linearly rise is ascribed to the flat band condition and therefore directly measures the SBH. This method requires that one SBH is much smaller than the other such that the conduction is unipolar and therefore can only measure one SBH. The extracted SBH also contains inherent uncertainty due to the interpretation of the flat band condition. The reason that authors are forced to use this method could be because of large tunneling currents present in these surface based devices. Because of the strong gate coupling from the dielectric oxide, the Schottky barrier will be thin in these devices and significant tunneling through the Schottky barriers will occur. The reverse bias leakage current of the Schottky diode will be a combination of tunneling and thermionic emission and the modeling will be complicated.

Suspended devices, on the other hand, have wider Schottky barriers and tunneling is suppressed. The lack of tunneling leads to a constant reverse bias leakage current of the Schottky diode, which gives rise to the current plateaus. The lack of tunneling is also evidenced by the plateaus being nearly independent of the gate voltages (Figure 3.7a), and this gate voltage independence means that our determinations of $I_{0,SBe}$ and $I_{0,SBh}$ are robust. Finally, this SBH measurement method improves on the previously mentioned method, because both the p-type and n-type Schottky barriers are simultaneously measured.

In conclusion, we have developed a general model for the I_{sd} - V_{sd} characteristics of suspended CNT split-gate devices. This model explains variations in the literature in the I_{sd} - V_{sd}

characteristics in terms of the metal WF and CNT diameter. The model is also used to extract the p-type and n-type SBHs from temperature dependent I_{sd} - V_{sd} measurements.

CHAPTER 4

Giant modulation of the electronic band gap of carbon nanotubes by dielectric screening

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4.1 Introduction

Carbon nanotubes (CNTs) are a promising platform to move integrated-circuit technology beyond the current limits of silicon.^{3,78,79} However, there are critical open questions regarding the nature of the transport band gap in CNTs, and in particular the role that electron correlations may play in determining this band gap. In quantum transport experiments,⁵⁸ electron-electron (e-e) interactions lead to phenomenon such as Luttinger liquid physics^{80,81} and Wigner crystal formation in CNTs,^{82,83} and may also explain anomalous spin-orbit coupling in CNTs,⁸⁴ and anomalous band gaps in nominally-metallic CNTs.⁸⁵ Beyond this low-energy physics typically observed at cryogenic temperatures, theoretical models suggest that electron correlations play a significant role in nanotube electronic properties even at room temperature. A giant renormalization of the single-particle gap (the transport gap) is predicted due to electron correlations. The key experimental signature of this effect is the relationship between the transport gap and the dielectric environment (Figure 4.1).⁸⁶



Figure 4.1. Theoretical calculation of the enhancement of the transport gap, $E_g/E_{g,bare}$, as a function of the effective dielectric constant, ϵ_{eff} . The calculations are performed for a narrow-gap and semiconducting CNTs with diameter a) D = 2 nm and b) D = 1 nm. $E_g/E_{g,bare}$ depends on diameter for narrow-gap CNTs, but not semiconducting CNTs. In experiment, ϵ_{eff} is controlled by the dielectric environment. The transport gap calculation is based on the random-phase approximation method,⁸⁶ and includes a contribution due to curvature (see Equation 4.2).

A screening dependent transport gap is particularly significant because a mutable gap would dramatically affect the design of nanoelectronic devices. In the CNT system, there is preliminary experimental evidence that such an effect exists. A scanning tunneling microscopy study showed that a semiconducting CNT in direct contact with the metal substrate had a 25% smaller transport gap than a similar CNT that, by chance, was positioned a few angstroms above the metal substrate.⁷⁴ In other experiments, *I-V* curves of pn junctions made from semiconducting CNTs have been interpreted in a framework of band gap renormalization.^{68,87} Screening-induced changes in transport gap have been confirmed in other low-dimensional nanomaterials. Recent experiments showed that single-layer MoSe₂ prepared on graphite had 11% smaller single-particle gap than single-layer MoSe₂ prepared on bilayer graphene.⁸⁸ In our current work, we demonstrate changes in the CNT transport gap greater than 30%, an extraordinarily large effect.

A theoretical framework for understanding the influence of dielectric environment on the transport gap of semiconducting CNTs was first developed by Ando.⁸⁶ This framework begins with the non-interacting model for CNT band structure, in which the "bare" transport gap is given by

$$E_{\rm g,bare} \approx 0.7 \, {\rm eVnm}/D,$$
 (4.1)

where *D* is CNT diameter. Ando predicted that this bare transport gap is enhanced by a factor of ~ 2 when e-e interactions are considered. The enhancement factor depends on the dielectric constant of environment surrounding the CNT, as illustrated in Figure 4.1. Ando predicted that changes in E_g could not be observed by optical measurements of absorption/emission resonances (exciton resonances) because exciton binding energy, E_b , also changes with dielectric screening. While Ando's theory describing the E_g in semiconducting CNTs has been corroborated by additional theoretical work,^{15,89–93} experimental verification of the relationship between E_g and dielectric environment has remained lacking.

In this work we also investigate the nature of the transport gap in narrow-gap CNTs (often called "metallic" CNTs). To facilitate comparison, we sometimes refer to semiconducting CNTs as wide-gap CNTs. Carbon nanotubes that are considered metallic based on a simple zone-folding approximation have a small curvature-induced gap. Without considering e-e correlations, the bare curvature-induced transport gap is calculated to be,⁵⁸

$$E_{\rm g,bare} \approx (50 \text{ meVnm}^2/D^2)\cos 3\theta,$$
 (4.2)

where θ is chiral angle. In our current work, we have extended Ando's theory to predict the enhancement of this curvature-induced transport gap in narrow-gap CNTs (Figure 4.1).

To test the predicted relationship between E_g and dielectric environment we developed in-situ methods to measure individual CNTs in various dielectric environments. Using individual ultraclean suspended CNTs (Section 3.2), we perform measurements before and after coating with solid dielectrics and submersion in dielectric liquids. Multiple techniques are used to determine the change in band gap and demonstrate the extraordinary sensitivity of CNT electronic structure to dielectric environment.

4.2 Solid dielectrics

We first explored the possibility of using metal oxides to coat the CNT and modify the dielectric environment. TiO₂ is particularly promising because of its high DC dielectric constant of approximately 100.^{94,95} TEM imaging has shown that electron-beam-deposited Ti metal will form a thin conformal coating on CNTs.⁹⁶ We deposited approximately 1 nm of Ti metal on our devices and let it oxidize in air to form a coating of TiO₂. Figure 4.2b shows the conductivity between two adjacent unconnected metal electrodes on the SiO₂ surface after metal deposition. Immediately after deposition, there is conductivity between the two electrodes as current flows through the thin layer of Ti metal. The conductivity exponentially decreases with time as the Ti metal oxidizes. The Ti should completely oxidize in an ambient environment because the native oxide thickness of Ti is 2.5 nm⁹⁷, but we facilitated the oxidation by putting the device in an oven at 200 C for 5 minutes. After annealing, the leakage current was not measurable. We further verified that the deposition does not damage the CNT with cross-sectional TEM imaging of CNTs grown on quartz (Figure 4.2c).



Figure 4.2 Oxidizing a 1nm thick film of Ti metal. a) Schematic of the measurement. b)
Current between two metal electrodes after deposition of the Ti as a function of time. c) Crosssectional TEM image showing a CNT grown on quartz and covered in a ~ 1 nm thick layer of
TiO₂. Image taken in collaboration with Pinshane Huang.

The effect of a 1 nm TiO₂ coating on the electrical properties of wide and narrow-gap CNTs is shown in Figure 4.3. For the wide-gap CNT, there is an overall increase in conductance and an emergence of n-type conductivity. For the narrow-gap CNT, the gate voltage no longer modulates the conductance. These observations are consistent with a reduction in the e-e interaction component of E_g . However, they are also consistent with an increase in electrostatic disorder.



Figure 4.3 $G(V_g)$ of an a) wide-gap and b) narrow-gap CNT before and after coating of approximately 1 nm of TiO₂.

Without e-e interactions, a cutting line through the Dirac point of the non-interacting graphene band structure determines the band structure of narrow-gap CNTs (Section 2.2). One hypothesis for the change observed in Figure 4.3b is that the e-e interaction component of the bandgap was dramatically reduced, and the remaining curvature and strain contributions to the bandgap were not sufficient to modulate the conductance at room temperature. In this theory, it should be possible to reintroduce the conductance modulation by applying a magnetic field down the axis of the CNT, even without an initial bandgap arising from curvature or strain. An axial magnetic field of magnitude B shifts the cutting lines by an amount $\Delta k_{\perp} = \frac{eD}{4\hbar}B$. This will lead to the opening of a bandgap $E_{\rm g} = 2v_F \frac{eD}{4}B$, where v_F is the Fermi velocity (Section 2.2).⁹⁸

To test this hypothesis we measured the low temperature conductance with a magnetic field applied along the axis of the CNT (Figure 4.4). There is a negligible difference in the conductance with and without a magnetic field, implying that the lack of conductance modulation is not simply due to a reduction in the bandgap.



Figure 4.4 Evidence of TiO₂ induced electrostatic disorder from low temperature I_{sd} - V_g measurements a) Low temperature I_{sd} - V_g of a narrow-gap CNT coated in TiO₂ with and without an axial magnetic field. b) Schematic band diagram of a narrow-gap CNT coated in TiO₂. The fluctuating electrostatic potential from the TiO₂ leads to alternating n-doped and p-doped regions. Electrons easily tunnel between these regions.

Electrostatic disorder was a factor in previous experiments that used SiO₂ substrates to investigate the effect of a dielectric substrate on narrow-gap CNTs.⁹⁹ Amer et al. compared pairs of CNT devices made from the same CNT, where the CNT was either suspended or touching the SiO₂ substrate. The substrate-bound CNT exhibited reduced transconductance; the high conductance wings in the $G(V_g)$ curve were suppressed, and the low-conductance dip was raised. Flattening of the $G(V_g)$ curve was explained by electrostatic disorder. It is known that SiO₂ substrates introduce a spatially-fluctuating disorder potential with magnitude ~ ± 100 meV.¹⁰⁰ This band bending occurs over atomic length scales. For narrow-gap CNTs the transmission through these kind of barriers will be near unity.¹⁰¹ In this situation, the transport of electrons through the system will not sensitively depend on the Fermi level position as shown in Figure 4.4b. We conclude that the TiO₂ coating introduces significant electrostatic disorder and obscures any signature of a changed bandgap.

For the case of the wide-gap CNT (Figure 4.3b), the appearance of n-type conductance and the increase in p-type conductance are promising evidence for a reduced E_g . However, the observations are also consistent with electrostatic disorder, which will 'blur' the conduction and valence band edges and broaden the range of gate voltages over which the semiconducting channel is conductive. This broadening of the band edges is also consistent with the reduced p-type normalized transconductance, where normalized transconductance is defined as dG/dV_g .

4.3 Liquid dielectrics

4.3.1 Non-conductive dielectric liquid (RIO)

In order to avoid the electrostatic disorder caused by solid dielectric coatings, we investigated liquid dielectrics. Figure 4.5c and Figure 4.5d show measurements of $G(V_g)$ for a narrow-gap and a semiconducting CNT, respectively. The $G(V_g)$ curves were first measured in air. The devices were then submerged in refractive index oil (n = 1.46, Cargille) and measured again. This measurement has been repeated on 4 additional narrow-gap CNTs, and 6 additional wide-gap CNTs. In the narrow-gap CNTs, the oil environment reproducibly increases *G* and the maximum value of the normalized transconductance. In the semiconducting CNTs, there is no conductance at $V_g > 0$, due to the Schottky barriers for n-type transport (Section 3.4). When $V_g < 0$ the conductance turns on very abruptly, both in air and oil environment.


Figure 4.5 Effect of refractive index oil on $G(V_g)$. a) Schematic of a CNT field-effect transistor in immersed in an oil environment. b) Conductance of a narrow-gap CNT in air and oil environments. c) Conductance of a wide-bandgap CNT in air and oil environments.

We first comment on the increase in peak transconductance in narrow-gap CNTs. When the device is submerged in oil, the oil increases the capacitive coupling between the back gate and the CNT. This increased gate capacitance means that more charge carriers are pulled into the CNT for a given V_{g} , consistent with our observations.

The increase in transconductance is one of several observations showing that the dielectric liquid does not introduce electrostatic disorder along the length of the CNT. In contrast to electrostatic disorder (Section 4.2), when liquid is added to narrow-gap devices, transconductance is increased (Figure 4.5c). We also note the sharp turn-on observed in semiconducting CNT devices both before and after submersion in liquid (Figure 4.5d). There is no evidence that the liquid causes a disorder tail in the transistor curve. This is a key insight. Dielectric liquids unlock the possibility of exploring the effect of dielectric screening without the complicating factor of electrostatic disorder.

The overall increases in *G* observed in Figure 4.5 suggests a reduction in E_g . For narrow-gap CNTs, the dip in conductance is related to the size of E_g .¹⁰² A reduction in E_g would increase the number of carriers that are thermally activated across the gap, thereby raising *G*. This interpretation is only qualitative, however, and in Section 4.4 we verify and quantify the change

in E_g for narrow-gap CNTs. The wide-gap CNT also shows a small increase in on-state conductance, but this does not consistently happen from device to device. However, in an ambient environment the p-type Schottky barrier is already very small. Reducing E_g would not dramatically change the p-type Schottky barrier height, and therefore not dramatically affect the on-state conductance. Other changes caused by the oil, such as a change in the metal work function, likely play as important role in changes of the on-state conductance. Measuring a change in E_g for wide-gap CNTs requires a different experimental method discussed in Section 4.5.

4.3.2 Electrolytic fluid (isopropyl alcohol + electrolyte)

We also used isopropyl alcohol as a dielectric liquid motivated by its large DC dielectric constant of 19. Figure 4.6 shows the $G(V_g)$ curves for a narrow-gap and wide-gap device before and after immersion in IPA. Similar to devices immersed in RIO, CNTs immersed in isopropyl alcohol show evidence of a decreased bandgap. The minimum conductance of the narrow-gap CNT increases from 0.1 to 0.2 e^2/h , similar to narrow-gap CNTs immersed in RIO. The wide-gap CNT exhibits an increased p-type conductivity (in addition to a threshold shift), but now also exhibits a large n-type conductivity.



Figure 4.6 Effect of IPA on $G(V_g)$. a) Conductance of a narrow-gap CNT in air and IPA environments. d) Conductance of a wide-bandgap CNT in air and IPA environments.

The emergence of n-type conductivity of the wide-gap CNT is consistent with a reduced E_g , but could also be explained by enhanced gate coupling from the dielectric liquid. The dielectric would compress the V_g axis by at most a factor of the dielectric constant. In air, the n-type conductivity of these devices in negligible, even for $V_g = +25$ V. In IPA, significant conductivity is observed even at $V_g = 1$ V $< \frac{25 \text{ V}}{19}$, indicating that the n-type conductivity cannot be entirely explained by an enhanced gate coupling.

The emergence of n-type conductivity can be explained by considering the width of the n-type Schottky barrier. In an electrolytic fluid like isopropyl alcohol, the application of a gate voltage in the fluid causes ions to accumulate near the CNT, electrostatically doping the CNT. The band profile of the Schottky barriers, which normally suppresses the n-type conductivity (Section 3.4), will be affected by this new gating mechanism. Specifically, the Debye screening length, λ_D , is the characteristic length over which an electrostatic potential is screened by the fluid. Therefore, λ_D will determine the width of the Schottky barriers at the metal-CNT contacts. λ_D is given by the expression,

$$\lambda_{\rm D} = \sqrt{\frac{\epsilon k_B T}{2e^2 N_{\rm A} C}},$$

where ϵ is the dielectric constant of the fluid, *T* the temperature, *N*_A is Avogadro's number, and *C* the ionic concentration (mole/m³). For sufficiently large ionic concentrations, tunneling through the Schottky barriers will be possible, resulting in the n-type conductivity. In Section 4.5, we will see that by increasing C, we can directly measure the transport bandgap of semiconducting CNTs.

4.4 Bandgap change in narrow-gap CNTs

The overall change in *G* for narrow-gap CNTs in an oil environment (Figure 4.5b) suggests either a change in E_g , or a change in the work function of the metal electrodes (Section 3.5). We first discuss the role of the metal work function and eliminate the possibility that a change in work function can explain Figure 4.5b.

We investigated the influence of the metal work function on device characteristics by modifying the surface adsorbates on the metal electrodes. Derycke et al. showed that a vacuum environment (clean metal surfaces) favors alignment between the metal's Fermi level and the conduction band of the CNT. In contrast, an ambient environment (water and oxygen adsorbates) favors alignment between the metal's Fermi level and the valence band of the CNT.¹⁰³ Figure 4.7 shows $R(V_g)$ curves that were obtained as a narrow-gap CNT is brought from a vacuum environment into an ambient environment. In vacuum, the n-type resistance is lower than p-type resistance, consistent with Fermi level alignment with the conduction band. After exposure to ambient environment, the p-type resistance is lower than n-type resistance. The biggest resistance peak is obtained while the device is transitioning from the vacuum to the ambient environment and $R(V_g)$ is perfectly symmetric (purple curve). While the $R(V_g)$ curve is clearly affected by metal work function (red, purple and black curves), submerging the device in oil (gray curve) has a much larger effect than can be explained by changes in the metal work function. We conclude that changes in metal work function can vary the resistance peak by ±10%, but cannot explain the dramatic reduction in resistance caused by the oil environment.



Figure 4.7 Resistance of a narrow-gap CNT measured with different metal WFs (red, purple and black curves). The same device measured in refractive index oil (dashed gray curve).

To quantify E_g before and after submersion in oil, we require a transport model that relates the $R(V_g)$ curve to E_g . We have taken an empirical approach to establishing such a relationship. We performed Coulomb blockade spectroscopy measurements to determine E_g for a set of 10 narrow-gap CNT devices. For each device we also measured $R(V_g)$ at room temperature. From this data set we find a strong correlation between E_g and the room temperature $R(V_g)$, as described below.

Coulomb blockade spectroscopy was performed in a vacuum environment at T = 2 K. The transport gap is resolved by measuring *I* while varying V_{sd} and V_g , as shown in Figure 4.8a and Figure 4.8c. Figure 4.8b and Figure 4.8d show the corresponding room-temperature measurements of $R(V_g)$ (air environment). The resistance peak is quantified using the parameter $\Delta R = R_{peak} - R_c$, where R_c is the contact resistance of the device. The contact resistance is determined by extrapolating the wings of the $R(V_g)$ curve, which asymptotically approach R_c in an exponential fashion.



Figure 4.8 Low-temperature and room-temperature transport for two narrow-gap devices. (a) and (c) show CB spectroscopy taken at 2 K. The lines follow the edges of the 0th diamond and are extrapolated to determine the bandgap. (b) and (d) show room temperature conductance along with R_{peak} and R_{c} .

Measurements of E_g and ΔR from 10 different narrow-gap CNTs are summarized in Figure 4.9a. A linear regression of $\ln(\Delta R)$ vs. E_g yields

$$E_{g} = [58.9 \text{ meV}] \cdot \ln\left(\frac{\Delta R}{[13.3 \text{ } k\Omega]}\right)$$

$$4.3$$

If ΔR measurements are used to estimate E_g (using Equation 4.3), the average residual error is 13 meV.



Figure 4.9 Quantifying the change in bandgap for narrow-gap devices. (a) Summary of ΔR and E_g values for 10 different narrow-gap CNT devices. The source-drain separation distance, *L*, varies from 300 nm to 2000 nm. (b) The transport gap, E_g , measured before and after submersion in refractive index oil (RIO), machine pump oil (MPO), and pure isopropanol (IPA). E_g is calculated from Equation 4.3 using measurements of ΔR . The devices are different from those presented in Figure 5a, and all have $L = 2 \mu m$, except for device 9 which has $L = 1.5 \mu m$. The estimated experimental error in determination of E_g is ±5% as determined from the measured variation in E_g with metal WF in Figure 4.7.

Surprisingly, our empirical fit is not improved by accounting for the length of the CNT channel. Insensitivity to channel length may be explained by considering band bending. Only a short segment of the CNT is maximally depleted of charge carriers. The high-resistance segment can be treated as a ballistic channel if the segment length is a few hundred nanometers in length (i.e. less than the scattering length in the narrow-gap CNT).

Using Equation 4.3 we quantify the reduction in E_g when narrow-gap CNTs are submerged in refractive index oil, machine pump oil (Hyvac, P8900-1) and isopropanol. The average reduction in E_g is 36% for refractive index oil, 19% for machine pump oil, and 26% for isopropanol.

4.5 Bandgap change in wide-gap CNTs

We now turn to wide-gap CNTs for which $E_g >> k_BT$. In these devices the peak resistance is too large to measure, therefore, E_g cannot be quantified using Equation 4.3. We adopt a different approach. To determine E_g in air we utilize chiral index identification and literature values for the first excitionic transition energy, S_{11} , and the exciton binding energy, E_b . To determine E_g in the dielectric liquid, we take inspiration from previous work on liquid-gated CNTs¹⁰⁴ and liquidgated WSe₂ devices.¹² We use a conducting liquid to gate our devices and determine the gatevoltage window where the CNT is depleted of charge carriers. This gate voltage window is then equated to E_g . The liquid gate medium is chosen to ensure that (1) The capacitive coupling between CNT and the gate is very strong, and (2) The Schottky barriers are sufficiently thin that the onset of p-type and n-type doping is observable.

Experiments on a wide-gap CNT are illustrated in Figure 4.10. We first determine the chiral index of the CNT by measuring the photocurrent spectrum in air (Figure 4.10a & b). From the photocurrent spectrum we identify the exciton resonances and compare to the exciton resonances listed in the CNT atlas.⁴⁵ We find excellent agreement between our measured resonances and the expected resonances for chiral index (20, 18). From the chiral index we know that the lowest energy exciton resonance (in air) is 400 meV.⁴⁵ We can also estimate the exciton binding energy, $E_{\rm b}$, associated with this first exciton resonance. Exciton binding in CNTs of various diameters was previously quantified using two-photon optical characterization of chirality-enriched CNT in a plastic thin film.¹⁰⁵ In a dielectric environment, $\epsilon_{\rm env} \sim 3$, the exciton binding energy in a 2.6-nm

diameter CNT is 130 meV. Therefore, 130 meV is a lower bound for E_b in air. We conclude that $E_{g,air} = S_{11,air} + E_{b,air} > 530$ meV.



Figure 4.10 Method of measuring the change in transport gap for wide-bandgap CNTs. a)
Schematic of the photocurrent spectroscopy measurement that is used to determine chiral index.
b) The spectral dependence of the photocurrent (red line) plotted together with the expected absorption cross section of a (20,18) CNT. c) Schematic of a liquid-gating measurement. d) *I*_{sd}-*V*_g in pure IPA (gray line) and salty IPA, 30mM of TBAF, (red line). Inset: Log plot of the sub-threshold region using salted IPA.

Next, the CNT is submerged in isopropanol and we measure $G(V_g)$. The gate voltage is applied to the liquid, rather than to underlying gate electrode. We are careful to minimize leakage currents between the liquid and the source/drain electrodes. Isopropanol is used for the liquid dielectric, rather than oil, because ionic species can be dissolved in the isopropanol. Dissolved ions are critical for increasing the gate capacitance, and shrinking the length of the Schottky barriers.¹² The liquid potential is measured by an independent electrode via a high-impedance voltmeter.¹² The light grey curve in Figure 4.10d is measured in pure isopropanol and the red curve is measured in salted isopropanol (30 mM tetrabutylammonium fluoride).

To verify that the Schottky barriers are sufficiently transparent, and the liquid gate capacitance is sufficiently strong, we measure the sub-threshold slope of the $G(V_g)$ curve (see inset to Figure 4.10d). In pure isopropanol we observe a sub-threshold swing $\sim 120 \text{ mV/dec}$. In salted isopropanol the sub-threshold swing is 60 mV/dec, the lowest possible value. A sub-threshold swing of 60 mV/dec indicates that there is a one-to-one relationship between the eV_g and the Fermi energy in the CNT when the Fermi energy is within the transport gap.

The transport gap is determined by extrapolating the linear regions of the $G(V_g)$ curve to the V_g axis.¹² The x-intercepts define a gate-voltage window of 0.42 V, suggesting that $E_g = 0.42 \text{ eV}$. We conclude that the isopropanol environment reduces E_g from > 0.53 eV to 0.42 eV. We repeated this experiment on two additional wide-gap CNTs (see Table 4.1). The average reduction from the lower bound value of $E_{g,air}$, to $E_{g,ipa}$ is 25%.

1410		, <i>E</i> g,air, and t	nen misoprop	allol, Eg,1pa. All u	evices have L - 2	. μΠ
	Device #	(<i>n</i> , <i>m</i>)	<i>d</i> (nm)	$E_{\rm g,air}$ (meV)	$E_{\rm g,ipa}$ (meV)	
	12	(20,18)	2.58	> 530	420	

Table 4.1 Modifying the transport gap of wide-gap CNTs. The transport gap was first characterized in air. $E_{\alpha air}$ and then in isopropanol. $E_{\alpha ina}$ All devices have L = 2 µm.

Device #	(n, m)	<i>d</i> (nm)	$E_{\rm g,air}$ (meV)	$E_{g,ipa}$ (meV)		
12	12 (20,18)		> 530	420		
13	(27,14)	2.83	> 540	380		
14	(26,10)	2.52	> 600	440		

4.6 Discussion

Our experiments in which the environment is changed from air and isopropanol reveal a 25% reduction in E_g for semiconducting CNTs and a 32% reduction in E_g for narrow-gap CNTs.

Comparing these percentages to theory (Figure 4.1), we conclude that our observations are consistent with ϵ_{eff} increasing from about $2\epsilon_0$ to $5\epsilon_0$. These values of ϵ_{eff} can be understood as follows. In the air environment, there is a small amount of screening from the CNT itself. Previous authors have estimated $\epsilon_{eff} \sim 2\epsilon_0$ for a CNT surrounded by air or vacuum.⁹¹ In the isopropanol environment, additional screening comes from the dielectric liquid. The dielectric response of the liquid is frequency dependent. At low frequency, $\epsilon_{env} = 18\epsilon_0$ and at high frequencies (visible light) $\epsilon_{env} = 1.9\epsilon_0$. The relevant frequencies associated with the e-e interactions that determine band gap renormalization are currently unknown. However, from our estimate of ϵ_{eff} in the isopropanol environment ($5\epsilon_0$), we postulate that GHz or THz frequencies are most relevant to the band gap renormalization process.

Band gap renormalization calculations (Figure 4.1) and our experiments both suggest that e-e interactions have a larger effect on narrow-gap CNTs than semiconducting CNTs. The renormalized band gap can be written as $E_g = E_{g,bare} + \Sigma$, where Σ describes the contribution of e-e interactions (Section 1.2.2). The scaling behavior of Σ is described by $E_{g,bare}$; $f(E_C/E_K)$, where the dimensionless factor f increases as a function of effective Coulomb energy, $E_C = e^2/\epsilon_{eff}D$, divided by typical kinetic energy E_K .¹⁰⁶ Typical kinetic energy is an order of magnitude smaller in narrow gap CNTs compared to semiconducting CNTs, due to the smaller band gap. Thus narrow-gap CNTs have a larger factor $f(E_C/E_K)$. This insight explains the larger enhancement factors for narrow gap CNTs (Figure 4.1), and the greater sensitivity of narrow gap CNTs to dielectric screening.

The transport gap, E_g , includes a Coulomb charging energy component, e^2/C_{tot} , where C_{tot} is the total capacitance between the CNT and the nearby metal electrodes (source, drain and gate). This charging energy is reduced when a suspended CNT device is submerged in dielectric liquid. Therefore, it is important to consider whether a change in Coulomb charging energy can account for the observed change in E_g . Coulomb blockade spectroscopy measurements reveal that the typical charging energy for our CNTs is no more than 15 meV (see Figure 4.8). Submerging a device in refractive index oil may reduce this charging energy by a factor of 3. Thus, a narrowgap CNT with initial $E_g = 200$ meV would be reduced to $E_g = 190$ meV in refractive index oil. Figure 5.8b shows that the experimentally observed changes in E_g are much larger. Therefore, the observed reduction in E_g cannot be explained by a simple change in charging energy.

In conclusion, we have demonstrated the experimental ability to tune the e-e interaction strength in CNTs while simultaneously monitoring transport properties. The effect of e-e interactions on the transport gap is remarkably large, verifying a long-standing theoretical prediction for semiconducting CNTs. We have extended this theoretical picture to narrow-gap CNTs and experimentally demonstrated the same effect in the narrow-gap CNTs. While it is well known that CNT transport properties are exquisitely sensitive to structural variables (i.e. diameter, chiral index, mechanical strain), our work shows that CNTs are also extremely sensitive to the polarizability of their environment. Knowledge of this environmental sensitivity is critical for rational design of CNT devices. Beyond the field of CNT science and technology, the strongly-correlated electron physics governing this transport gap enhancement likely affects other low-dimensional systems that are currently under investigation.^{107,108}

CHAPTER 5

Photocurrent Quantum Yield in Suspended CNT pn junctions

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5.1 Introduction

Nanomaterials are promising candidates for improving the performance of photodetectors and solar energy harvesting devices. Unique features of nanomaterials such as quantum confinement and strong electron-electron interactions can be harnessed to enhance the conversion of electromagnetic energy into electrical current. For example, the multiple exciton generation process in quantum dots has been used to boost the quantum efficiency of solar cell devices,^{25,109} and evidence of carrier multiplication (CM) has been observed in carbon nanotube (CNT) photodiodes.²

Carbon nanotubes are particularly promising because CM has been observed close to the energy conservation limit ($\hbar \omega = 2E_g$, where $\hbar \omega$ is photon energy and E_g is the CNT band gap).² Experiments conducted at low-temperature (T = 60 K) on individual CNTs show that reversebias photocurrent increases dramatically when a CNT photodiode is illuminated with $\hbar \omega > 2E_g$ rather than $\hbar \omega < 2E_g$. While compelling, these experiments did not quantify the photocurrent quantum yield (PCQY), defined as the number of photogenerated carriers extracted from the device per absorbed photon. Robust methods of determining PCQY are needed to examine the physics of CM in CNTs.

One previous report has estimated the photocurrent PCQY of CNT photodiodes. Malapanis et al. measured individual CNT photodiodes in photovoltaic mode (no reverse bias) and found a room temperature photocurrent PCQY of 1 - 5%.³⁷ The photodiodes used by Malapanis et al. were built from partially suspended CNTs with diameters in the range 1 - 2 nm. The whole device was illuminated, including the CNT-to-metal contacts. Photon energy was tuned to the first and second exciton transitions (S₁₁ and S₂₂).

In this work, we study CNT pn junctions in a different regime. We use fully-suspended individual CNTs with diameters of 2 - 3 nm. The optical excitation energy is tuned to either S_{44} or S_{55} and we study PCQY as a function of reverse bias. Using a focused laser spot, we directly measure the length of the intrinsic region and isolate photocurrent from the pn junction. We find a photocurrent PCQY of 20 - 40%, an order of magnitude larger than previous work and a step closer to the ultimate goal of exceeding 100%.

5.2 Spatial photocurrent



Figure 5.1. The effect of the n-type Schottky barrier on the optoelectronic characteristics of the CNT split-gate device. a) Dark and illuminated diode curves from device 1 (red and black respectively). The illumination wavelength is 632nm and $V_{g2} = -V_{g1} = 8$ V. b) Scanning photocurrent microscopy image of device 1, $V_{g2} = -V_{g1} = 8$ V and $V_{sd} = 0$ V. The dotted line indicates the CNT axis. The black dashed lines indicate the source/drain electrode edges. The gray dashed lines indicate the split-gate electrode edges. The beam radius a = 550 nm. The scale bar is 1 µm.

Figure 5.1a shows the dark and illuminated diode curves of a device measured in air with $V_{g2} = -V_{g1} = 8$ V. Illumination is performed with a defocused laser such that the CNT and metal

electrodes are uniformly illuminated. The dark curve has already been described in detail in Chapter 3. The illuminated curve is strikingly different from a traditional photodiode. At negative bias, the photocurrent increases linearly with V_{sd} . At positive bias, between 0.1 – 0.6 V, the photocurrent also increases linearly with V_{sd} . The open circuit voltage, $V_{oc} \sim 50$ mV, is much lower than the band gap of a semiconducting CNT.

To understand the cause of these unusual characteristics, we performed scanning photocurrent microscopy (SPCM) using our home-built SPCM system.¹¹⁰ A focused laser spot is raster scanned over the surface while the reflected light and photocurrent, I_{PC} , are measured simultaneously (Section 1.3.4). The laser spot has a Gaussian intensity profile, $\exp(-r^2/a^2)$ where r is the distance from the center of the beam and a is the beam radius. Figure 5.1b shows the scanning photocurrent microscopy (SPCM) image at $V_{sd} = 0$ with a = 550 nm. The negative photocurrent in the center of the CNT coincides with the expected position of the pn junction. The positive photocurrent near the right contact is close to the junction between the n-doped CNT and the metal electrode. The pattern in the photocurrent image (positive and negative spots elongated in the y-direction) is consistent with the superimposition of two Gaussian point spread functions of opposite sign centered 0.9 µm apart.

The zero-bias SPCM data implies that there is a pn junction in the center of the suspended CNT and a Schottky diode where the n-type CNT meets the metal electrode. This data, taken in an ambient environment, is consistent with the diode model described in Chapter 3. We further tested the model by repeating SPCM measurements at different values of V_{sd} . Figure 5.2 shows photocurrent profiles measured along the CNT axis. At x = 0 the laser is centered on the middle of the suspended CNT. At $x = \pm 1.1 \ \mu m$ the laser is centered on the ends of the suspended CNT.

When $V_{sd} > 0$, the photocurrent peak at $x = 0.9 \ \mu\text{m}$ is enhanced. When $V_{sd} < 0$, the photocurrent peak at x = 0 is enhanced. When $V_{sd} = 0$, the two peaks are roughly equal.



Figure 5.2. Photocurrent cross-sections (gray dots) measured along the CNT axis of device 1. The Gaussian beam radius is a = 550 nm. The laser is scanned with a step size of 60 nm. Solid black lines show fit curves constructed from Gaussian functions (a = 550 nm) centered at x = 0and x = 0.9 µm. The bias voltages are a) $V_{sd} = +0.25$ V, b) $V_{sd} = 0$ V, and c) $V_{sd} = -0.25$ V.

The band bending diagrams accompanying Figure 5.2 illustrate our interpretation of the photocurrent peaks at x = 0 and 0.9 µm. The intrinsic regions of along the CNT will be the only photoactive regions, because Auger processes lead to extremely short minority carrier lifetimes in doped CNTs.^{111,112} When $V_{sd} = +0.25$ V, the peak centered at x = 0.9 µm dominates $I_{PC}(x)$. The n-type Schottky barrier is in reverse bias, which increases the length of the intrinsic region near the contact, L_{Sch} . When $V_{sd} = -0.25$ V, the peak centered at x = 0 dominates. The pn junction is in reverse bias, which increases the length of the CNT, L. Fits to the photocurrent cross sections are included in Figure 5.2, which accurately predict the

changing photocurrent profile by changing the intrinsic region lengths of the pn and Schottky diodes (black bars). The expression used for the fits is derived in the next section.

5.3 Spatial photocurrent model

The fits in Figure 5.2 are generated by combining the spatial photocurrent response of the pn junction and the Schottky barrier. In this section, we develop the fitting function by deriving the spatial photocurrent response for an isolated intrinsic region of a pn junction (Figure 5.3).



Figure 5.3. Schematic representation of the convolution of a focused laser spot with the intrinsic region of a pn junction. The graphs show a schematic representation of, from top to bottom, the photon flux profile, PCQY (η) model, band diagram, and resulting photocurrent profile.

We are interested in the photocurrent response that results from a Gaussian laser beam positioned at x_b with respect to the center of the intrinsic region (x = 0). The photon flux, is given by,

$$\Phi(x, x_{\rm b}) = \Phi_0 e^{-(\frac{x - x_{\rm b}}{a})^2} .$$
(5.1)

where $\Phi_0 = \frac{P}{\pi a^2 E_{\text{ph}}}$, *P* is the total power contained in the laser spot, *a* is the beam radius, and

 $E_{\rm ph}$ is the photon energy. The beam radius, *a*, is determined from fitting a photocurrent cross section perpendicular to the CNT. The central peak of the Airy distribution is fit with a Gaussian. This procedure effectively ignores the side lobes and assumes the entire *P* in contained within the central peak, overestimating Φ_0 and therefore producing a lower bound of the PCQY. As a working model, we assume the following position dependent photocurrent PCQY, $\eta(x)$,

$$\eta(x) = \begin{cases} \eta_0 & -\frac{L}{2} < x < +\frac{L}{2} \\ 0 & |x| > \frac{L}{2} \end{cases},$$
(5.2)

where L is the length of the pn junction intrinsic region. We will now determine the photocurrent $dI_{PC}(x,x_b)$ arising from an infinitesimal section dx of CNT located at the position x. The photocurrent depends on two processes happening one after the other, charge generation and charge extraction. The charge generation will be proportional to $\Phi(x, x_b)$ multiplied by the effective absorption cross section $\sigma_c N' dx$, where σ_c is the absorption cross section per atom, and $N'==\frac{4\pi d}{\sqrt{3}\alpha^2}$ the number of carbon atoms per unit length, where d is the CNT diameter. The charge extraction efficiency is described by $\eta(x)$ and

$$dI_{\rm PC}(x,x_{\rm b}) = e\Phi(x,x_{\rm b})\eta(x)\sigma_c N'dx.$$
(5.3)

Integrating Equation 5.3 along the length of the CNT gives the total photocurrent, $I_{PC}(x_b)$. Using the model for $\eta(x)$ given in Equation 5.2,

$$I_{\rm PC}(x_{\rm b}) = e\sigma_{\rm c} N \eta_0 \Phi_0 \int_{-\frac{L}{2}}^{\frac{L}{2}} e^{-(\frac{x-x_{\rm b}}{a})^2} dx.$$
(5.4)

The integral can be calculated with the definition of an error function $\operatorname{erf}(x) = \frac{1}{\sqrt{\pi}} \int_0^x e^{-x'^2} dx'$,

$$I_{\rm PC}(x_{\rm b}) = A\eta_0 \left(\operatorname{erf}\left(\frac{x_{\rm b} + \frac{L}{2}}{a}\right) - \operatorname{erf}\left(\frac{x_{\rm b} - \frac{L}{2}}{a}\right) \right), \tag{5.5}$$

where $A = \frac{\sqrt{\pi}}{2} a e \sigma_c N' \Phi_0$ is a constant for a given CNT chirality and photon energy.

The fits in Figure 5.2 model the spatial photocurrent response as a combination of the pn junction photocurrent, $I_{PC,pn}$, arising from an intrinsic region centered at x_{pn} and the Schottky diode photocurrent, $I_{PC,Sch}$, arising from an intrinsic region centered at x_{Sch} with length L_{sch} . The combined photocurrent, $I_{PC,tot}$, will be

$$I_{\rm PC,tot}(x_{\rm b}, x_{\rm pn}, x_{\rm Sch}) = I_{\rm PC,pn}(x_{\rm b}, x_{\rm pn}) + I_{\rm PC,Sch}(x_{\rm b}, x_{\rm Sch}),$$
(5.6)

where,

$$I_{\text{PC,pn}}(x_{\text{b}}, x_{\text{pn}}) = -A\eta_{0,\text{pn}}\left(\text{erf}\left(\frac{x_{\text{b}} - x_{\text{pn}} + \frac{L}{2}}{a}\right) - \text{erf}\left(\frac{x_{\text{b}} - x_{\text{pn}} - \frac{L}{2}}{a}\right)\right)$$
(5.7)

$$I_{\text{PC,Sch}}(x_{\text{b}}, x_{\text{Sch}}) = + A\eta_{0,\text{Sch}}\left(\operatorname{erf}\left(\frac{x_{\text{b}} \cdot x_{\text{Sch}} + \frac{L_{\text{Sch}}}{2}}{a}\right) - \operatorname{erf}\left(\frac{x_{\text{b}} \cdot x_{\text{Sch}} - \frac{L_{\text{Sch}}}{2}}{a}\right)\right).$$
(5.8)

 $\eta_{0,\text{pn}}$ and $\eta_{0,\text{Sch}}$ are the PCQY of the pn junction and Schottky barrier, respectively. The direction of the local electric field determines the sign of the current. For sufficiently small bias the intrinsic region lengths will be sufficiently small and we can make the approximation L_{Sch} , L < a.

$$I_{\rm PC,Sch}^{\rm peak} \approx + \frac{A}{\sqrt{\pi}a} \eta_{0,\rm Sch} L_{\rm Sch}$$
(5.9)

$$I_{\rm PC,pn}^{\rm peak} \approx -\frac{A}{\sqrt{\pi a}} \eta_{0,pn} L \tag{5.10}$$

In summary, $I_{PC,Sch}$ and $I_{PC,pn}$ have opposite sign due to the opposing local electric fields. $I_{PC,Sch}$ grows when $V_{sd} > 0$ because L_{Sch} increases. $I_{PC,pn}$ are when $V_{sd} < 0$ because L increases. Near $V_{sd} = 0$, $I_{PC,pn}$ and $I_{PC,Sch}$ become equal and opposite. The model depicted in Figure 5.2 helps explain the illuminated diode curve shown in Figure 5.1a. The illuminated diode response from another device is shown in Figure 5.4a. This measurement uses a defocused laser (uniform Φ_0 across the whole device), which leads to a net photocurrent $I_{PC,pn}(V_{sd}) + I_{PC,Sch}(V_{sd})$. Adding these opposing photocurrents results in three distinct segments of the illuminated I_{sd} - V_{sd} curve. At negative V_{sd} , the net photocurrent is dominated by $I_{PC,pn}$. At positive V_{sd} , the net photocurrent is dominated by $I_{PC,pn}$. At positive V_{sd} , the net photocurrent is dominated by $I_{PC,pn}$. When V_{sd} is close to zero, the two photocurrents oppose each other. These three V_{sd} regimes appear as three different slopes in the illuminated diode curve. Figure 5.4b and Figure 5.4c show schematically how the addition of $I_{PC,pn}(V_{sd})$ and $I_{PC,Sch}(V_{sd})$ lead to the measured response.



Figure 5.4 a) Illuminated (red) and dark (black) diode curves for device 4. b) Schematic representation of the pn junction photocurrent (orange) and the Schottky barrier photocurrent (blue) as a function of V_{sd} . c) The resulting total photocurrent.

In the context of photocurrent PCQY measurements, the key insight is that $I_{PC,pn}$ dominates when $V_{sd} < 0$. The disappearance of $I_{PC,Sch}$ indicates a flat band condition where the n-type CNT meets the electrode. We conclude that a small negative V_{sd} is ideal for studying the photocurrent generation process in the suspended CNT pn junction. Reverse bias is used for this purpose throughout the rest of this paper. For a sufficiently large reverse bias, $I_{PC,Sch} \approx 0$ and Equation 5.6 reduces to

$$I_{PC,tot}(x_{\rm b}, x_{\rm pn}, x_{\rm Sch}) = -A\eta_{0,\rm pn}\left(\operatorname{erf}\left(\frac{x_{\rm b} - x_{\rm pn} + \frac{L}{2}}{a}\right) - \operatorname{erf}\left(\frac{x_{\rm b} - x_{\rm pn} - \frac{L}{2}}{a}\right)\right)$$
(5.11)

Our goal is to extract the photocurrent PCQY from the pn junction by fitting photocurrent profiles in reverse bias to Equation 5.11. We determine $I_{PC,pn}$ and *a* from SPCM imaging. Determination of the wavelength dependent absorption cross section $\sigma_c N'$, the photon flux Φ_0 , and the intrinsic region length *L* is discussed below.

5.4 The photon flux

The photon flux, Φ , includes contributions from both incident and reflected light, and is complicated by interference effects. This interference can be observed readily by measuring the spectrally-dependent photocurrent under defocused illumination with light polarized perpendicular to the CNT axis (Figure 5.5a). The absorption cross section for perpendicularly polarized light is spectrally flat,¹¹³ but a spectral dependence is observed in the photocurrent spectrum. This spectral dependence arises from constructive (~2.2 eV) and destructive (~2.6 eV) interference between the incident beam and reflected beam from the gate electrodes (Figure 5.5b).



Figure 5.5 Observing the intensity enhancement effect. a) Spectrally-dependent photocurrent with incident light polarized perpendicular to the CNT, along with an intensity enhancement factor calculated from Equation 5.15 using h = 720 nm. b) Schematic representation of the interference of incident light with the reflected light from the gate electrodes. The figure shows the standing wave that results from the superposition of the incident and reflected light for the two photon energies indicated in part a.

Figure 5.5 includes a wavelength-dependent intensity-enhancement factor (IEF), $\frac{|E|^2}{|E_0|^2}$, calculated from the simple model presented below. *E* and *E*₀ are optical electric fields determined at the CNT position when the device structure is respectively present or absent. The electric field is determined a height *h* above a reflecting surface with an incident plane wave source. The reflected light will travel a distance 2*h* before returning to the CNT.

$$E = E_{\text{incident}} + E_{\text{reflected}} \tag{5.12}$$

$$E = E_0 (1 + r e^{i(\phi_r + 2k_y h)})$$
(5.13)

 k_y is the component of the wavevector perpendicular to the surface and ϕ_r is the phase shift acquired from reflection off of the substrate. We are interested in the magnitude squared of *E*,

$$|E|^{2} = |E_{0}|^{2} (1 + r^{2} + 2r\cos(\phi_{r} + 2k_{y}h))$$
(5.14)

Assuming a perfect conductor, $\phi_r = 90^\circ$ and r = 1

$$\frac{|E|^2}{|E_0|^2} = 2(1 + \cos(2k_y h))$$
(5.15)

The CNT can sag below the level of the electrodes¹¹⁴ and the effective height of the CNT can vary from device to device. Matching the interference minima allows for a determination of the CNT height 720 nm above the trench for this particular device.

Expressing Equation 5.15 in terms of k_y allows the plane wave to be incident at an angle, which is relevant when using a microscope objective to illuminate the device. For all microscope objectives, there is a portion of the light incident to the surface at an angle. This is particularly important when we use a reflective objective. In the measurement with the refractive objective, the device is illuminated with light from the center of the defocused photocurrent spot. In this portion of the beam the light is incident normal to the surface and $k_y = k$. Reflective objectives, on the other hand, work by reflecting light off a central mirror that then reflects of secondary mirrors to send the light onto the surface at an angle (Figure 5.6c). The angle of incidence, θ , can roughly be determined by the numerical aperture of the objective, $NA = n \sin \theta$, where n = 1 is the index of refraction. For our reflective objective NA = 0.5 and therefore, $k_y \approx k \cos(30^\circ)$. Figure 5.6a and Figure 5.6b show the photocurrent spectrum from the same device measured with a reflective and refractive objective using light polarized parallel to the CNT axis, respectively. The changes in the photocurrent spectra modeled well using $k_{y,refl} = k_{y,refr} \cos(30^\circ)$.



Figure 5.6 Spectrally-dependent photocurrent taken with a a) refractive and b) reflective objective. The calculation of the IEFs utilize the same parameters except that $k_{y,refl} = k_{y,refr} \cos(30^\circ)$. c) Schematic of a reflective objective. The light is incident on the surface at an angle of approximately 30°.

The simple plane wave model predicts locations of the maxima and minima well but a more quantitative IEF is required for an accurate determination of the PCQY. In our method of determining the PCQY, the beam is tightly focused over the center of the CNT and the plane wave approximation is not valid. The Pt electrodes are also not perfect conductors and complex phase shifts upon reflection will occur. Finally, geometric effects are important when the wavelength approaches critical dimensions of the device (~ 1 μ m). To model the IEF more accurately we performed FDTD simulations with LumericalTM software. Figure 5.7a shows a spatial map of a FDTD simulation with a plane wave source with a wavelength that causes constructive interference at the location of the CNT.



Figure 5.7) a) Visualization of the spatially dependent intensity enhancement factor calculated in an FDTD simulation. The incident light is a plane wave with wavelength of 1 µm, is polarized perpendicularly to the CNT, and is incident normal to the surface. b) Schematic of the device structure used in the simulation.

We have performed simulations for both a defocused and focused laser (Figure 5.8c). The defocused beam is relevant for understanding the photocurrent spectrum (Figure 5.8a), while the focused beam is used to interpret the SPCM measurements. The calculated IEF accurately predicts the suppression of photocurrent at photon energies near 1.8 eV and 2.6 eV (Figure 5.8a), compared to the calculated $\cdot \sigma_{\rm C}(\hbar\omega)$ for this chirality (See Section 5.5). The CNT height is set 675 nm above the reflecting surface of the split-gate electrodes to match the interference minima and maxima. Comparing $\frac{|E|^2}{|E_0|^2} \cdot \sigma_{\rm C}(\hbar\omega)$ (dashed line in Figure 5.8a) to the measured photocurrent spectrum reveals excellent agreement in the energy range 1.5 - 3 eV, giving us confidence in our understanding of the IEF. The discrepancy at low photon energy is suggestive of reduced η . The energy dependence of η is discussed further in Section 5.7.



Figure 5.8 Comparing the Photocurrent spectrum and the absorption cross seciton. a)
Photocurrent current spectrum measured from device 1 (solid line). Calculated photocurrent
spectra based on absorption cross section and intensity enhancement factor (dashed line). The
photocurrent measurement is performed with a defocused laser spot of (*a* ~ 10 µm). b)
Calculated (solid line) and energy-averaged (dashed line) absorption cross section. c) Calculated
intensity enhancement factor for focused beam (solid line) and plane wave (dashed line).

5.5 Absorption cross section

The photocurrent spectrum (Figure 5.8a) is used to determine the chiral index, which is used to calculate $\sigma_c(\hbar\omega)$. The excitonic peak positions are extracted from the photocurrent spectrum and compared to the CNT Atlas⁴⁵ to determine the chirality. Specifically, the accuracy of the fits for different chiralities are sorted by the residual energy per peak $\sum_i \frac{E_{exp,i}^2 - E_{atlas,i}^2}{N_{peaks}}$, where N_{peaks} is the

number of peaks extracted from the spectrum, $E_{\exp,i}$ are the experimentally measured peak positions, and $E_{\text{atlas},i}$ are the peak positions calculated from Equation 2.11. After identifying the chiral index that matches the observed exciton resonances, $\sigma_{c}(\hbar\omega)$ is calculated using Equation 2.12. The calculated absorption spectrum for Device 1 (parallel polarization) is plotted in Figure 5.8b.

This method of chiral identification is similar to our previously published technique of identifying the chiral index of CNTs in suspended CNT field-effect transisitors¹¹⁵, but there are improvements in the method that should be mentioned. First, the residual error is normalized by the N_{peaks} , which allows for more consistent measure of the accuracy of the chiral identification between measurements that include different numbers of peaks. Secondly, the measured resonance energies are compared to the results of Equation 2.11, instead of the experimental atlas data. The experimental atlas data often only had two resonances for a given chirality. Using a full set of resonance energies for each chirality improves the accuracy and allows for the ruling out of incorrect chiralities that might happen to have two peaks in common with the experimental data.

5.6 Intrinsic region length

To determine the length of the intrinsic region, *L*, we maximize the spatial resolution of our SPCM by reducing the beam radius (Appendix 8.4). The measurements are performed in a vacuum environment to minimize gate hysteresis effects. Interestingly, the vacuum environment has an additional benefit of reducing the photocurrent generated at the n-type Schottky barrier when the device is operated at $V_{sd} = 0$ V. The reduced effect of the Schottky barrier is likely due to a change in metal work function (Section 3.5.2).¹¹⁶ Figure 4a shows an image obtained with $V_{sd} = -0.5$ V and a = 0.37 µm. The photocurrent spot is symmetric and corresponds to the point

spread function of the laser. The faint halo around the main photocurrent spot is caused by the Airy disk pattern generated by overfilling the back plane of the objective (Appendix 8.4). When the reverse bias is increased, the photocurrent spot elongates along the CNT axis, suggesting an increase in *L*. We quantify *L* by comparing the photocurrent profile, $I_{PC}(x)$, to the expected profile from an intrinsic region of length *L*.



Figure 5.9 a-b) High resolution photocurrent images of device 3 (100X objective). In this measurement, $a = 0.37 \mu m$, $V_{g2} = -V_{g1} = 10 V$, $P_{laser} = 1.56 \mu W$, and $\hbar \omega = 2.54 eV a$) $V_{sd} = -0.5 V$, b) $V_{sd} = -4 V$. Scale bars are 1 μ m. c) Photocurrent cross-sections at $V_{sd} = 0$, -0.5, -1, -2, -3, and -4 V (red dots). Fitted curves using Equation 5.11. Inset: Curve fitting parameters.

We obtain good fits to the SPCM cross sections by assuming η is independent of V_{sd} and adjusting *L* for each curve. The resulting values of η and *L* are shown in the inset of Figure 4c. There are other approaches to fitting the data, for example, leaving both η and *L* as free parameters when $L > 0.37 \mu m$. These alternative fitting procedures lead to qualitatively similar results.

The constant η hypothesis results in a near perfect linear relationship between *L* and V_{sd} (see inset Figure 5.9). This linear relationship between *L* and V_{sd} is consistent with the illuminated diode curve (Figure 5.1a) and can be explained using a simple electrostatic model (also see Section 1.3.2). The integral of the electric field across the pn junction depends on V_{sd} and E_{g} ,

$$\int \mathcal{E}(x)dx = \alpha V_{\rm sd} - E_{\rm g}/e, \qquad (5.16)$$

where $\mathcal{E}(x)$ is the component of electric field pointing along the CNT axis, and α is the fraction of V_{sd} that drops across the pn junction. The magnitude of $\int \mathcal{E}(x)dx$ grows when V_{sd} becomes more negative. The integral is approximately equal to the product $\mathcal{E}_{max}L$, where \mathcal{E}_{max} is the maximum value of $\mathcal{E}(x)$. \mathcal{E}_{max} depends strongly on V_{g1} , V_{g2} and the charge density profile along the CNT, but has relatively weak dependence on V_{sd} (there is no appreciable change in the charge density profile when $|V_{sd}| \ll |V_{g1,g2}|$). Therefore, we expect the linear relationship between in $\mathcal{E}_{max}L$ and V_{sd} to be driven by L, while \mathcal{E}_{max} stays constant. Based on the experimentally determined relationship between L and V_{sd} (inset of Figure 5.9) we estimate $\mathcal{E}_{max} \approx -4 \text{ V/}\mu\text{m}$ for the gate voltages used here. A similar electric field strength was recently calculated by solving Poisson's equation iteratively to find a self-consistent charge density profile in a suspended CNT device with $V_{g2} = -V_{g1} = 9 \text{ V}$.¹¹⁷

5.7 Results

After establishing robust methods to determine $\sigma_C N'$, Φ_0 , and L, we measured η in three devices (Table 5.1). The supercontinuum light source was polarized parallel to the CNT axis and tuned to an exciton resonance (either S_{44} or S_{55}). The intensity was reduced below 1 kW/cm² to

ensure that measurements are performed in the linear regime. At higher laser powers we have observed sub-linear power dependence, as reported by other authors.¹¹⁸ A reverse bias $V_{sd} = -4$ V was used to make *L* and I_{peak} more experimentally accessible.

Table 5.1 Determination of photocurrent PCQY, η , when $\hbar\omega = S_{44}$ or S_{55} . I_{peak} was measured with a 50X objective (NA = 0.5) and $V_{\text{sd}} = -4$ V, $V_{g2} = -V_{g1} = 10$ V. η is calculated using Equation 5.11. CNT band gap is estimated using $E_g = S_{11} + X_b$, where $X_b \approx 340$ meV \cdot nm/D is the

Device	(n, m)	D	E_g	$\hbar\omega =$	$\sigma_{\rm c} N'$ (nm)	Power	$ E ^2$	a	L	Ipeak	η
		(nm)	(eV)	\mathbf{S}_{xx}		(µW)	$ E_0 ^2$	(µm)	(µm)	(pA)	
1	(20, 19)	2.65	0.53	2.34 eV	0.358	4.21	1.42	0.48	1.25	415	0.44
				$= S_{55}$							
2	(22, 9)	2.17	0.63	2.13 eV	0.401	3.29	1.65	0.55	1.64	241	0.23
				$= S_{44}$							
3	(18, 17)	2.37	0.59	1.92 eV	0.460	3.19	0.61	0.58	1.07	134	0.29
				$= S_{44}$							
3	(18, 17)	2.37	0.59	2.54 eV	0.322	2.51	0.78	0.42	1.07	138	0.49
				$= S_{55}$							

exciton binding energy in the first sub band.¹⁰⁵

We find that η is approximately 0.3 for the conditions we have studied. This result has implications for understanding the energy relaxation pathways in CNTs. The relaxation process is expected to occur on the femptosecond timescale,⁴⁴ three orders of magnitude faster than the escape time from the pn junction.¹¹⁸ The photoexcited S_{44} (or S_{55}) excitons will decay into low energy excitons (S_{11}) and free carriers in the first sub-band ($e_1 + h_1$). Theoretical work predicts that S_{11} production is strongly favored over $e_1 + h_1$ production.¹¹⁹ While transient absorption spectroscopy experiments at room temperature show that multiple S_{11} excitons can be created from a single photon,¹²⁰ only a fraction of S_{11} excitons will be dissociated by \mathcal{E} and contribute photocurrent.¹²¹ An additional mechanism for CM in CNTs is impact ionization by free carriers that are accelerated by \mathcal{E}^2 .² However, impact ionization is not expected to persist at room temperature due to phonon friction.¹²² In summary, we speculate that our experiment generates a large population of S_{11} excitons, but a smaller population of $e_1 + h_1$ which results in a photocurrent PCQY less than 1.

Table 1 shows a trend toward higher η at higher photon energy. For S_{44} excitation, the average η is 0.24. For S_{55} excitation the average η is 0.41. An increase in η with $\hbar\omega$ is consistent with CM mechanisms, i.e. the excess photon energy $\hbar\omega - E_g$ is directed into increased carrier generation. A similar observation of relative changes in PCQY was reported by Kazaoui et al.¹²³

The increase in η at higher excitation energies may partially explain our higher PCQY values compared to earlier measurements by Malapanis et al. (these previous measurements used S_{11} and S_{22} excitation).³⁷ Additional differences that may contribute to our higher PCQY values include larger diameter CNTs (exciton binding energy ~ 1/*D*) and our experimental method that directly measures *L* and mitigates the effect of $I_{PC,Sch}$. They also used a different device geometry in which the CNT was partially suspended and partially in contact with the SiO₂. They calculated the axial electric field distribution of these devices and found it was only significant at the edge of the trench in the SiO₂. Therefore, photogenerated carriers had to diffuse to the edge of the SiO₂ before being dissociated. In addition, their doped regions were longer and back scattering of carriers could have reduced the PCQY.

In conclusion, we have developed a robust method to determine photocurrent PCQY from individual CNT pn junctions. We observe photocurrent PCQY values in the range 20 - 40% in suspended CNT pn junctions measured at room temperature with built-in electric field ≈ 4 V/µm. It is likely that multiple S_{11} excitons are also generated during the photoexcitation process, but are not registered in our photocurrent measurement. Enhancement of photocurrent PCQY from impact ionization processes is likely suppressed at room temperature. Our results set a new benchmark for the performance of CNT pn junctions in photodetector and energy harvesting applications. Promising directions for future work include increasing electric field strength, decreasing temperature, and modifying the dielectric environment to reduce exciton binding.⁹¹ With optimized conditions, CNTs show promise for achieving photocurrent PCQY greater than unity.

CHAPTER 6

Conclusion

6.1 Summary

This work forms the foundation for exploring e-e interactions in CNTs through the experimental platform of the suspended CNT split-gate device. We have developed an understanding of the electronic and optoelectronic response of these devices, and used this understanding to begin exploring the effects of strong e-e interactions in CNTs.

The ultimate goal for the suspended CNT split-gate devices is to explore and optimize carrier multiplication. However, in order to understand how the CNT split-gate device behaves under optical excitation, we should understand how the device behaves in the absence of light. In Chapter 3, we started by developing and understanding of electronic transport in the suspended split-gate CNT devices. Specifically, we investigated the behavior of the device when operated as a CNTFET and as a diode. By measuring diode curves while changing the metal work function, we were able to develop a detailed equivalent circuit model of the split-gate devices. This chapter lays the foundation of understanding the device physics of the CNT split-gate devices that is necessary for the following chapters.

The same e-e interactions that drive CM also drive bandgap renormalization, therefore the two effects are inseparable and both must be understood. In Chapter 4 we studied how the bandgap of a CNT is affected by immersion in a dielectric environment. We showed that the transport gap, normally a fixed material property in bulk semiconductors, is dramatically affected by the strength of e-e interactions. Specifically, we showed that the transport gap of both narrow-gap and semiconducting CNTs is reduced approximately 30% upon immersion in a dielectric.

Finally, in Chapter 5 we explore the optoelectronic properties of the CNT pn junction. Using scanning photocurrent microscopy, we determined that the Schottky barriers are a major detriment to the device efficiency. However, utilizing insights developed in Chapter 3, we determine that applying a reverse bias can overcome the detrimental effect of the Schottky

barrier. We then develop a method to extract the quantum yield of photocurrent generation from the scanning photocurrent microscopy images. We achieve a quantum yield approximately an order of magnitude larger than previously observed in the literature.

6.2 Achieving a PCQY > 100%

The immediate direction of future research is optimizing the PCQY of the CNT pn junction above 100%. As discussed in Section 5.7, it is possible that already more than one exciton is created per photon, but only a fraction of those excitons dissociate into free electron-hole pairs. We should then be able to achieve a PCQY > 100% by enhancing the dissociation of the photogenerated excitons. The main way to achieve a greater dissociation of excitons is to increase the axial electric field as shown in Figure 6.1. The exciton dissociation rate as a function of axial field has been theoretically studied by Perebeinos et al.¹²⁴



Figure 6.1 Enhancing exciton dissociation with an axial electric field. The electric field on the right is strong enough to pull apart the electron-hole pair, which can now result in a photocurrent.

Experimentally, a larger axial electric field can be achieved by increasing the magnitudes of the split-gate voltages. Figure 6.2 shows a preliminary work studying how to enhance exciton dissociation using this method. Figure 6.2a shows photocurrent cross sections for increasing values of $V_{g1} = -V_{g2}$. Initially, as the gate voltage is increased, the peak photocurrent increases as
predicted from Figure 6.1. However, the intrinsic region also shrinks because of the stronger electric field at higher gate voltages (Section 5.6). Above $V_{g1} = -V_{g2} = 15$ V, the width of the photocurrent cross section shrinking and the peak photocurrent also stops increasing. Figure 6.2c and Figure 6.2d show the PCQY and *L* extracted from the fits to equation 5.11, respectively. Both the PCQY and *L* are free parameters in the fit. Below $V_{g1} = -V_{g2} = 15$ V, the PCQY increases and *L* decreases. Above $V_{g1} = -V_{g2} = 15$ V, the PCQY plateaus at approximately 100% and *L* approaches the beam waist, *a*.



Figure 6.2 Preliminary data of PCQY as a function of $V_{g1} = -V_{g2.}$ a,b) Photocurrent cross sections. In part b the cross section visibly stays the same with increasing $V_{g1} = -V_{g2.}$ c) The extracted PCQY and d) intrinsic region length from the fits to the photocurrent cross sections in parts a and b. Both PCQY and L are free parameters in the fits.

One explanation for the plateau in PCQY is that as *L* has been decreased significantly smaller than the beam waist. When $L \ll a$, the photocurrent cross section will have the same cross section as the laser beam, and the peak photocurrent will scale linearly with *L*. Fitting a cross

section with L < a, the fit will set $L \sim a$ and compensate the magnitude of the cross section by changing the PCQY. Therefore, the unchanged photocurrent cross section could represent a nearcancellation of an increasing PCQY and decreasing intrinsic region length. In this interpretation, we would conclude PCQY > 100%. Further work is needed to understand how the fitting behaves when L < a to verify the above interpretation of the intrinsic region length.

It is also possible that the data in Figure 6.2d is accurate. The electrostatic model of equation 5.16 predicts that $L \sim 1/V_g$, which fits reasonably well to the data. Self-consistent electrostatics modeling of the CNT pn junction is needed to give a more accurate $L(V_g)$ model. Finally, It is possible that hysteresis,^{125–129} which becomes more severe at higher gate voltages is constraining the effective gate voltage experienced by the CNT.

Another exciting direction of research is studying the optoelectronic properties of these devices in a liquid dielectric. Interesting optoelectronic phenomena should occur when the CNT is immersed in a dielectric.¹³⁰ However, the dielectric may also be another useful tool for enhancing exciton dissociation. The dielectric would reduce the exciton binding energy (E_b) by reducing the e-e interaction strength (Section 1.2.4). In addition, the dielectric would simply increase the achievable axial electric field by increasing the CNT-gate capacitance. Figure 6.3 shows preliminary data of PCQY measurements before and after immersion in a dielectric liquid. The PCQY is increased after immersion, even after taking into account the changes in intensity enhancement factor that arise from the different index of refraction.



Figure 6.3 PCQY measurements in refractive index oil. The change in IEF (Section 5.4) with the dielectric is taken into account. The photographs on the right show a chip with and without refractive index oil. The oil is wicked away before measurement to leave a thin and flat layer that does not distort SPCM measurements.

Reducing the strength of the e-e interactions has the potential to increase the PCQY by reducing E_b , but might also have detrimental effects such as suppressing carrier multiplication (CM). Because the rate of CM and E_b both depend on the strength of the e-e interactions, reducing E_b could also suppress CM. However, an interesting possibility is that these two processes are screened at different frequencies. Therefore, a dielectric material with a well-designed frequency dependent dielectric constant could strongly screen exciton binding but weakly screen the CM process. A natural choice for the relevant screening frequencies can be constructed by considering the timescales of the relevant processes. Carrier multiplication should occur on a femptosecond⁴⁴ timescale (10¹⁵ Hz) and exciton recombination in suspended CNTs occurs on the timescale of about 100 picoseconds¹³¹ (10¹⁰ Hz). Essentially, we would want a fluid that would not be able to polarize before CM occurred, but then would polarize before recombination.

In conclusion, there are many promising pathways to achieving a PCQY of greater than 100% and plenty of interesting physics to explore along the way.

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CHAPTER 8

Appendix: SPCM

8.1 Overview

The spectrally-tunable scanning photocurrent microscope (SPCM) allows us to spatially and spectrally map the optoelectronic response of a nanoscale device. Figure 8.1 shows an overview of the SPCM. Devices are connected electrically through connection with probe needles or wire bonding to a chip holder. The combination of scanning mirrors and parabolic mirrors position a focused laser spot at an arbitrary position on a surface. By monitoring the photocurrent and reflected light as a function of the laser position, we can map the local photocurrent response relative to the position of metal electrodes. The laser source can be tuned from 400-1800 nm, allowing us to examine the optoelectronics of CNTs over a wide energy range. Table 8.1 outlines the manufacturers and part numbers of the SPCM components.



Figure 8.1 Overview of the scanning photocurrent microscope.

Part	Manufacturer	Part number
Supercontinuum laser	Fianium	SC-450
Double monochromator	Princeton Instruments	DSP-2150
Scan mirrors	Nutfield Technology	OHF-7
Scan mirrors servo amplifier	Nutfield Technology	QD-4000
Parabolic mirrors	Thorlabs	MPD254508-90-P01
Photodiode	Thorlabs	PDA100A.
Refractive objective (100X)	Nikon	80 CF45 Plan ELWD Epi 0
Refractive objective (50X)	Nikon	CFI LU Plan BD ELWD A
Reflective objective	Thorlabs	LMM-40X-P01
Preamp	Stanford Research Systems	SR570
Cryostat	Janis	ST-500

Table 8.1 Manufacturers and part numbers for the SPCM components

8.2 Laser source



Figure 8.2: Top) photograph and bottom) schematic of the light generation system.

Figure 8.2 shows an outline of the light generation system. To motivate the laser source used in this study, recall the absorption cross section of CNTs discussed in section 2.4. The absorption is concentrated in excitonic peaks and the energies of these peaks are highly dependent on the chiral index of the CNT. The chiral index of CNTs obtained from our growth process cannot be controlled and therefore the resulting excitonic resonance energies are unpredictable. To optically excite a CNT at an arbitrary excitonic resonance of an arbitrary chirality we require a collimated narrow bandwidth laser source that is tunable over a wide range of photon energies. We accomplish these requirements by filtering a supercontinuum white light laser through a double monochromator.

The supercontinuum laser starts with a low power pulse generated in a core pumped Yb-doped fiber with a repetition rate of 40 Mhz and pulse duration of 4ps centered around 1064 nm. The pulses amplified in a double clad Yb-doped fiber pumped by a high power laser diode (PUMA), and then sent into a highly nonlinear optical fiber. The intense laser pulses undergo a variety of different nonlinear optical affects in the fiber, which broadens the spectrum to 400-1800 nm. To filter the white light to a narrow bandwidth (~ 1 nm), the laser beam is passed through a double monochromator. Figure 8.2 shows the resulting power spectra measured before and after the monochromator.



Figure 8.3: Details of the light generation system. a) optics of beam expansion b) beam path through the monochromator c) beam position on parabolic mirror to counteract dispersive aberrations.

Figure 8.3a shows the path the light takes into the monochromator. First, a pair of parabolic mirrors expands the beam size. Increasing the size of the beam means that it will fill the back of the objective, giving better resolution (Section 8.4). By performing beam expansion before the monochromator, we minimize degradation of the monochromator gratings from the intense laser pulses. However, the beam can become too large in the IR so flip mirrors provide an alternative pathway where the beam will not be expanded (dashed line, Figure 8.3a). When not expanding the beam in the IR, a low pass filter is placed in the beam path to reduce the power on the gratings. The low-pass filter also ensures that second order diffraction peaks from short wavelength photons do not enter the IR beam.

The light is then focused into the monochromator through an entrance slit (Figure 8.3b). After passing through the slit the light is directed onto a cylindrical mirror to be collimated and sent onto the grating. The grating causes a diffraction pattern, which is then directed by another mirror onto a slit (not visible in picture). Controlling the angle of the grating precisely with a motor will send a specific wavelength of light, in this case green light, through the slit, blocking the other wavelengths. The width of the center slit is chosen to give a good balance between a narrow bandwidth and total transmitted power. After passing through the center slit, the light passes through a second monochromator configured to be a mirror image of the first monochromator in order to counteract any dispersive effects.

Cylindrical mirrors are used in the process of directing the beam through the monochromator, which can cause the beam to become elliptical as it traverses the optics table. A useful trick is to counteract this elliptical aberration by using the asymmetry present in the parabolic mirror. The beam is purposefully bounced off the corner of the parabolic mirror (Figure 8.3c). This gives a symmetric beam profile at the back of the microscope objective. Future users of the SPCM may wish to try using cylindrical mirrors rather than the corner of a parabolic mirror.

8.3 Scanning photocurrent microscope



Figure 8.4 Operation of the SPCM. Top: photograph of the SPCM. Bottom: Schematic of the SPCM with reflection (R) and photocurrent (I_{PC}) data from a CNT split-gate device operating as a photodiode.

Figure 8.4 shows the SPCM which comprises the combination of scan mirrors, parabolic mirrors, and objective. The SPCM delivers a focused spot onto the sample surface at a desired location. First, the beam, coming from the monochromator, passes onto the galvanometer scan mirrors. The angle of the scan mirrors is controlled with a servo amplifier, which sends the beam out at an arbitrary angle toward a pair of parabolic mirrors. The parabolic mirrors are designed to send the beam into the aperture of the microscope objective, regardless of the beam angle from the scan mirrors.

Figure 8.5 shows an optical diagram of the working principle of the parabolic mirror pair. The parabolic mirrors have been replaced by simple glass lenses in this figure. Using parabolic mirrors instead of lenses complicates the alignment, but the principle is the same. To understand the design, recall that a ray originating from the focal point will exit a lens parallel to the optical axis, and vice versa. The scan mirrors are placed at the left focal point of the first lens. The center of the beam will therefore exit the first lens parallel to the optical axis, regardless of the angle of the scan mirrors. However, the first lens will focus the edges of the collimated beam. The purpose of the second lens is to recollimate the beam. This can be accomplished by placing the second lens a distance $d = f_1 + f_2$ away from the first lens. In the end, a collimated beam exits the second lens directed toward its focal point, where the aperture of the objective is placed.



Figure 8.5 Optical diagram of the SPCM. In our experimental setup we use parabolic mirrors instead of lenses to avoid chromatic aberrations, but the principle is the same.

Controlling the angle of the scan mirrors will control the angle at which the beam to enters the objective and the position of the focused spot will move across the surface. The reflection from the surface is diverted with a beam splitter (Figure 8.4) and monitored with a photodetector. Raster scanning the angle of the scan mirrors will therefore form a reflection image. The reflection of a suspended CNT split-gate device is shown in Figure 8.4. The reflection image

shows two large metal electrodes separated by a 2 μ m gap. A square of Fe catalyst, from which a CNT is grown, can be seen near the electrode edge. The texture on the electrode arises from degradation that occurs during the high temperature of the growth process. The other lines are gate electrodes that run underneath the electrode gap to electrostatically dope the CNT in to a pn junction.

The photocurrent response is simultaneously measured with the reflection (Figure 8.4d). The photocurrent is measured with a preamp. The reflection image calibrates the location of the focused laser spot with reference to the device structure. There is a single photocurrent spot arising from an individual carbon nanotube that has grown across the gap in the electrodes. In this image, the photocurrent is zero except for a spot centered in the middle of the CNT axis. This spatial photocurrent response is described in more detail in Chapter 5.

8.4 Photocurrent imaging tips

One of the most important characteristics of the SPCM is the point spread function of the focused spot. Achieving a tightly focused spot, for example, allows for resolution of smaller intrinsic region lengths (Section 8.4). The beam profile can be directly imaged by decreasing the length of the intrinsic region such that $L \ll a_{beam}$, and the intrinsic region is effectively point source of photocurrent.



Figure 8.6 The effect of overfilling the objective. a) SPCM photocurrent image and b) crosssection along the CNT axis when the objective is over-filled. C) SPCM photocurrent image and b) cross-section when the objective is under-filled.

Figure 8.6 shows the photocurrent images of a CNT device with a short *L* when the collimated beam profile underfills or overfills the back of the objective. The profile of the focused spot will be related to the incoming beam profile through a Fourier transform.¹³² Under-filling the back of the objective, the aperture will 'see' most of the Gaussian beam profile, and the Fourier transform of a Gaussian results in a Gaussian spot. By overfilling the back of the objective, the aperture is uniformly illuminated, and the resulting Fourier transform is a Bessel function or airy disk. The central peak of the airy distribution can still be approximated with a Gaussian fit. The FWHM extracted from a Gaussian fit is smaller for the overfilled beam profile than the Gaussian profile. However, the tighter focus comes at the price of 'side lobes' that develop. When the laser spot is centered on the CNT the side lobes are pushed onto the electrodes and do not

interfere much with the current. This gives a higher resolution along the length of the CNT when the objective is overfilled. This may affect the beam profile at large reverse bias.

The tighter focused central airy peak is due to a higher relative fraction of light entering the edge of the objective. This light, which is incident to the surface at a higher angle, has a larger k_{\perp} vector. k_{\perp} determines the spatial frequency along the surface and therefore the resolution. The airy distribution can be characterized by the distance of the first side lobe from the central peak, r. The minimum value of r can be written in terms of the light's wavelength λ and the numerical aperture of the objective, $NA = nsin(\theta)$, where

$$r = \frac{1.22\lambda}{2NA}$$

 θ is the maximum incident angle of light from the objective. Therefore, another way to decrease further the radius of the airy disk is to increase the numerical aperture. Figure 8.7 shows reflection images taken from two different NA objectives. The image taken with the NA 0.8 objective is sharper than that of the NA 0.5.



Figure 8.7 SPCM reflection images using an a) 50X and b) 100X objective.

Choosing a suitable scan rate (frequency of scan lines) is also critical for achieving good images. The preamp is designed to automatically apply a low pass filter to the input signal for

high sensitivity measurements. The cutoff frequency of the filter depends on the sensitivity and is applied even if the user-selectable filtering is turned off. The scan rate must be kept sufficiently low, depending on the image size, such that the filters do not affect the measurement. Figure 8.8 shows images taken at two different scan rates. The trailing effect observed in Figure 8.8a is caused by the filtering from the preamp.



Figure 8.8 SPCM photocurrent images with different scan rates. a) The scan rate (15 Hz) is too fast for the filters of the preamp causing 'streaking' of the photocurrent. b) Slowing the scan rate (5 Hz) fixes the problem.

8.5 Cryostat

Many important optoelectronic characteristics of CNTs depend on temperature. Gabor et. al. observed in their devices that carrier multiplication (CM) was suppressed above ~80K.² Theorists predicted that the suppression of CM was due to phonon friction from thermally excited phonons.¹²² However, the presence of thermally excited phonons may to increase the quantum yield of photocurrent generation through phonon assisted exciton dissociation.¹¹⁷ To access the interesting low temperature optoelectronic physics we use a Janis optical cryostat

(Figure 8.9). This chapter outlines work developing the low temperature measurement capabilities.



Figure 8.9 Photograph (left) and schematic (right) of the cryostat. The sample is separated from the temperature sensor, which can cause inaccurate temperature readings.

The built-in temperature sensor in the optical cryostat is a few cm away from the sample (Figure 8.9). In order to determine the temperature at the sample we placed a silicon diode in a sample holder. The measured temperature is shown by the red dots in Figure 8.10b. When the temperature sensor on the bottom is reading 77°K the sample temperature sensor reads 100°K. This temperature discrepancy is bad for liquid nitrogen measurements but is prohibitive for liquid helium measurements, which may be necessary to observe CM.



Figure 8.10 Improving the coupling of the sample holder and temperature sensor with clips. The clips can be seen at the edge of the chip holder in part a. b) Temperature at the sample holder, as measured by a temperature sensor wire bonded into the sample holder, versus the cryostat's internal temperature reading with and without the clips. C) CNT I_{sd}-V_{sd} characteristics at different temperatures. Achieving the ideal diode behavior at low temperature requires low temperature annealing.

To solve the problem of temperature discrepancy we fabricated clips to hold the chip holder in better thermal contact with the cold finger. The metal clips can be seen with screws holding down a sample holding chip can be seen at the edge of the cryostat window in Figure 8.10a. The green dots in Figure 8.10b show the temperature as measured by the silicon diode chip with the clips attached. Improving the thermal contact of the sample holder greatly improves the agreement between the sample holder and the cryostat temperature sensor. Now, when the temperature sensor on the bottom is reading 77 °K the sample temperature sensor reads 80 °K. The difference in sample temperature is apparent in the CNT pn junction diode measurements of Figure 8.10c. Diode curves are steeper at lower temperatures (Section 1.3).

Without the clips, thermal grease can applied between the sample holder and cold finger. Apiezon N has a particularly low vapor pressure and maintains thermal conductivity at low temperature, but above 300 °K will degrade and permanently contaminate the cryostat. The cryostat is rated to 475 °K and therefore this grease prohibits heating of the sample which is useful for facilitating the removal of surface adsorbates. The cryostat does use Krytox LVP for some mechanical joints, which can withstand heating at 475 °K.

The glass opening shown in Figure 8.10a allows for optical access. However, the cover glass also changes the resolution of the laser spot. Figure 8.11 shows the image of a CNT split-gate device with and without the cryostat cover glass above the sample. Future users of the SPCM may want to try using microscope objectives with cover glass correction to avoid this problem.



Figure 8.11 SPCM reflection images a) with and b) without the cryostat cover glass. Images were taken with the 100X refractive objective.

The cryostat is also useful at room temperature as vacuum environment. The vacuum environment reduces hysteresis which will reduce screening of the gate electrodes, which will increase the quantum yield (Section 6.2). In addition, the vacuum environment can remove adsorbates from the surface of the metal electrodes and change their work function (Section 3.5).