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Scanning Probe Characterization of Electronic Scattering in a One-Dimensional Conductor

DOCTOR OF PHILOSOPHY

in Physics

by

Elliot James Fuller

Dissertation Committee:
Professor Philip G. Collins, Chair
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Professor Regina Ragan

2015
DEDICATION

To my father, William Robert Fuller, who taught me that tinkering can lead to great things.
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”Scanning Probe Characterization of Electronic Scattering by Carbon Nanotube Defects” Fuller, E.J.; Hunt, S.R.; Corso, B.L.; Collins, P.G.; *APS March Meeting* Boston, MA March 2012 (presentation)
ABSTRACT OF THE DISSERTATION

Scanning Probe Characterization of Electronic Scattering in a One-Dimensional Conductor

By

Elliot James Fuller

Doctor of Philosophy in Physics

University of California, Irvine, 2015

Professor Philip G. Collins, Chair

The International Roadmap for Semiconductor Devices calls for transistors that will extend into the low-dimensional regime. As electronic devices are shrunk to increasingly lowered dimensions, the restricted geometry and extremely low carrier density results in an extraordinary sensitivity to interfaces, defects and disorder. This sensitivity is a significant barrier to their use in future technologies as it sufficiently alters their electronic properties so that their transport physics is no longer well understood. In this work, electronic scattering due to contacting electrodes, supporting substrates, defects and disorder is investigated in the case of field effect transistor (FET) devices composed of one-dimensional, single-walled carbon nanotubes (SWNTs). In order to investigate the various mechanisms of electronic scattering in SWNT FETs, scanning probe microscopy (SPM) techniques are developed in order to spatially resolve and distinguish each scattering mechanism. This dissertation gives a brief introduction to low-dimensional conductors in Chapter 1 and outlines basic experimental methods for characterizing SWNT FETs in Chapter 2. Next, the development of SPM techniques are described in Chapters 3 – 4, 6 and their application to understanding transport in SWNTs is described in Chapters 5 – 7.

The SPM techniques described in this dissertation are based upon Kelvin probe force microscopy (KPFM) and scanning gate microscopy (SGM). Chapter 3 describes modifications
to an existing atomic force microscope (AFM) electronics to increase the imaging speed of KPFM in order to extend it into a transport spectroscopy. Next, Chapter 4 describes a new KPFM technique, Parameterized-KPFM, that was developed to quantitatively measure the voltage gradients associated with electronic scattering in SWNT FETs. Finally, Chapter 6 describes extending the SGM technique into a spectroscopy called scanning gate spectroscopy (SGS) in order to investigate a SWNT’s local sensitivity to electric fields. Both the KPFM and SGS techniques were used to investigate FETs with pristine SWNTs, and those with SWNTs containing a single defect site.

In the first study, described in Chapter 5, KPFM was used to measure voltage gradients associated with diffusive electronic scattering along pristine SWNTs. The KPFM technique allowed for an accurate separation of SWNT resistance from the contact resistance that was greatly improved compared to previous work. The voltage gradients directly determined the inelastic mean free path $\lambda$ as a function of applied bias. At a temperature of 185 K, $\lambda$ was found to decrease from nearly 1 $\mu$m at low bias to 100 nm at high bias. Fitting $\lambda$ to established transport models determined the relative roles of substrate induced, surface polar-phonon scattering and SWNT optical phonon scattering. The optical phonon mean free path for spontaneous emission was found to be 62 \( \pm \) 20 nm at 300 K, significantly longer than observed in previous experimental studies and in much better agreement with theoretical predictions.

In another study, described in Chapter 7, KPFM was used to investigate SWNTs with defects. Single, covalent type defects were incorporated into pristine SWNTs by the method of electrochemical point-functionalization. Electronic scattering at defect sites was characterized by a combination of two-terminal transport spectroscopy and KPFM over a wide range of temperature and bias. Both transport measurements and KPFM were used to independently confirm high-resistance depletion regions that can extend to 1.0 $\mu$m in width surrounding a single defect. Fitting transport measurements to models demonstrated that
conductance through such wide depletion regions occurs via a modified, 1D version of Poole-Frenkel emission. The Poole-Frenkel model suggests that conduction through the depletion region is mediated by at least one or more localized defect trap states. The Poole-Frenkel trapping potential was found to be relatively weak with effective barrier heights measured to be $10^{-40}$ meV.

Finally, Chapter 6 discusses the use of SGS to investigate similar types of covalent defects. Point-functionalization of SWNTs in water, sulfuric acid, or hydrochloric acid produced single defect sites with different chemistries. Using SGS, the defect’s sensitivity to electric fields was measured and used to extract the energy-dependent transmission function. The three defect chemistries were distinguished by a spectroscopic fingerprint found in each transmission function.
Chapter 1

Introduction

1.1 Conduction in lowered dimensions

For many decades physicists and engineers have been struggling to answer an intriguing question: "How do electrons conduct through a material as we shrink its dimensions to microscopic length scales?" According to Ohm’s law, for a cuboid conductor of length $L$, height $H$ and width $W$, the electrical resistance $R$ can be written as

$$R = \rho \frac{L}{HW},$$  \hspace{1cm} (1.1)$$

where $\rho$ is the material’s bulk resistivity. How small can we scale $H$ or $W$ before this equation begins to break down? What new physical properties will emerge?

Eq. 1.1 begins to break down when a conductor’s dimensions are scaled below three impor-
tant characteristic lengths\textsuperscript{1}. The first important length is the electron de Broglie wavelength $\lambda_F$ which is a function of its kinetic energy. The next is the inelastic mean free path $\lambda_{MFP}$, which is the average length an electron travels through a material before losing momentum. Finally, the phase-relaxation length $\lambda_\phi$ is the average distance an electron travels before its quantum mechanical phase is destroyed. These lengths can have orders of magnitude differences for various materials and temperatures. For example, in typical Si based semiconductors $\lambda_{MFP}$ can be tens of nm, whereas in certain GaAs systems it can extend to mm length scales at low temperature \cite{29}.

Figure 1.1: A cartoon of a bulk conductor (a) and hypothetical low-dimensional systems: a two-dimensional plane (b), a one-dimensional wire (c) and a zero-dimensional, single state (d).

Fig. 1.1 depicts several hypothetical conductors in which one or more dimensions are missing or have been scaled down. Low-dimensional conductors are an extreme case in which one or more of the lengths in Eq. 1.1 has been shrunk to the atomic scale. At the scale of individual atoms, electrons are confined to below the $\lambda_F$ for a typical material and as a consequence the electron energy states become quantized and their behavior must be described using the laws of quantum mechanics. Here, classical transport breaks down and new transport

\textsuperscript{1}Although many physical properties can cause Eq. 1.1 to break down this discussion will be focused on how scale influences transport.
models must be considered.

One of the most successful models for understanding transport in low-dimensional systems is the Landauer-Büttiker formalism which breaks down the resistance problem into a quantum mechanical scattering problem \[17\]. The Landauer formula for resistance is simply

\[
R = \frac{\hbar}{2e^2 M T} = \frac{\hbar}{2e^2 M} + \frac{\hbar}{2e^2 M} \frac{1 - T}{T},
\]

where \(M\) is the number of quantized energy modes in the conductor and \(T\) is the probability for an electron to transmit from one end of the conductor to the other. Notice that this equation does not depend directly on the conductor dimensions \(H, W\) or \(L\), but instead depends on them indirectly through the number of quantized energy modes \(M\). Another important consequence is that despite ballistic conduction \((T = 1)\) the resistance of the conductor is not zero, but finite and quantized in units of \(\hbar/2e^2\).

One of the most effective introductions to the Landauer formalism is to consider the case of a one-dimensional conductor for which the quantum mechanical scattering problem can be solved exactly \[17\]. In this case, it can be shown that the transmission formalism leads to an intuitive description of resistance. Typically, this is done by using it to derive Ohm's law for series resistance in the limit of phase decoherence.

Consider two conductors with transmission probabilities \(T_1\) and \(T_2\) connected in series. This case is depicted diagrammatically in Fig. 1.2 (a). For simplicity, consider the case when the phase of the electrons is destroyed between each of the conductors. It is tempting to write the total transmission as \(T = T_1 T_2\), however the possibility of reflections between each of the scatters must be considered. In this case, the total transmission probability can be written
Figure 1.2: A diagram depicting quantum mechanical transmission and reflection between two conductors in series (a). If the phase is destroyed between the two conductors, the total transmission $T$ through the system can be written as a sum of all possible transmission and reflection probabilities (b).

as a sum of all possible transmissions and reflections as depicted in Fig. 1.2 (b). In total, $T$ is written as

$$T = T_1 T_2 + T_1 T_2 R_1 R_2 + T_1 T_2 R_1^2 R_2^2 + \ldots$$

$$= \frac{T_1 T_2}{1 - R_1 R_2}, \quad (1.3)$$

where we have invoked rules for a geometric series in the final step. By considering that
\( R_1 = 1 - T_1 \) and \( R_2 = 1 - T_2 \) we can rewrite Eq. 1.3 entirely in terms of transmission,

\[
\frac{1 - T}{T} = \frac{1 - T_1}{T_1} + \frac{1 - T_2}{T_2}.
\] (1.4)

Eq. 1.4 can be easily generalized to the case of many scatterers in series. This demonstrates that the total transmission \( T \) can be determined by a simple sum of the transmission probabilities of the constituent scatterers. By inserting Eq. 1.4 directly into Eq. 1.2 we recover the familiar Ohm’s law for series resistance, plus a small additional factor \( \frac{h}{2e^2 M} \). This factor is usually considered as part of the conductors contact resistance \( R_C \) and is negligible for bulk conductors.

\[
R = \frac{h}{2e^2 M} + \frac{h}{2e^2 M} \left( \frac{1 - T_1}{T_1} + \frac{1 - T_2}{T_2} + ... \right)
= R_C + R_1 + R_2 + ...
\approx R_1 + R_2 + ...
\] (1.5)

More generally, the quantum mechanical phase must be considered for devices with \( L \approx \lambda_\phi \) and Eq. 1.5 is not valid. However, Eq. 1.5 is still valid in the case that the \( L \approx \lambda_{MFP} \) and \( \lambda_{MFP} >> \lambda_\phi \). This is the case for the work presented in this dissertation and so Eq. 1.5 is of primary interest.
1.2 Low-dimensional materials

Low-dimensional electronic systems are the subject of intense scientific research. As early as the 1960s, physicists at IBM discovered that electrons could be confined to a two-dimensional (2D) space at the inversion layer of a bulk semiconductor transistor [38]. Confined to 2D, these electrons exhibited quantum electron transport that challenged the current understanding of the electronic states of matter [176, 101]. Driven by these exciting properties physicists began looking for other low-dimensional systems. Recently, newly discovered low-dimensional materials made of carbon have captivated the interest of scientists around the world. The element carbon has the unique property that it exists in an unusually wide variety of conductive allotropes that span the range of dimensions from bulk three-dimensional (3D) graphite all the way to zero-dimensional (0D) C\textsubscript{60} [63]. Fig. 1.3 depicts various allotropes of carbon including several low-dimensional varieties.

In 1991, shortly after the discovery of C\textsubscript{60} [96], Sumio Iijima discovered one-dimensional (1D) conductors made entirely of carbon called single-walled carbon nanotubes (SWNTs) [129, 70]. These hollow cylinders were only about 1 nm in diameter but could be grown to cm lengths. Theorists predicted extraordinary electronic properties [3] and exotic 1D physics [53, 177, 34] that had never before been accessible experimentally. This led to a scientific rush to isolate SWNTs and integrate them into working electronic devices for study [24].

A similar rush occurred again in 2004 when Andre Geim and Konstantin Novosolev successfully isolated graphene, a 2D carbon conductor only a single atom thick [128]. Graphene has similar properties to SWNTs, but many predicted that the 2D material would be more amenable to integration into working technologies [52]. Very soon after the isolation of graphene, it was discovered that other conductive 2D materials could be isolated with atomic scale thickness [127]. Currently, there is a growing field emerging around the study of "van der Waals heterostructures" composed of atomically thin crystal layers sandwiched together
by the van der Waals force [51].

Figure 1.3: Carbon allotropes including (a) diamond (b) graphite (c) 2D graphene (d) 0D $C_{60}$ (e) 1D single-walled carbon nanotube. Image credit M. Ströck [171].

Scientists are fascinated with low-dimensional conductors because they have very unusual electronic properties that are different from bulk. For example, they poorly screen electric fields due to their extremely low density of free carriers. As a consequence of poor screening and reduced dimensionality, Fermi-liquid theory can break down and electron-electron interactions and many-body effects become important. This has led to the fractional quantum hall effect observed 2D systems [176, 101] and Luttinger-liquid effects found in 1D [177, 31]. Additionally, the lack of screening causes many low-dimensional conductors to be extremely sensitive their environment. As a result their electronic properties can be tailored by introducing defects or by chemical functionalization [52, 27, 54].
1.3 A one-dimensional conductor: single-walled carbon nanotubes

The focus of this work is the study of electronic resistance in the case of SWNTs. SWNTs are an ideal system for investigating electronic scattering in the quasi-1D limit. At only 1–2 nm in diameter, SWNTs confine charge carriers to an extreme scale where quantum effects can dominate up to room temperature [31]. The electronic subbands created by such extreme confinement are separated by more than 0.5 eV so that under moderate bias only the lowest energy band can contribute to transport. Although there exists a degeneracy at the Fermi level that allows for four channels of conduction, coupling between these channels is weak enough that SWNT transport is considered to be very nearly 1D [107, 108, 117, 23].

Figure 1.4: The atomic structure for a zig-zag (semiconductor), armchair (metallic) and a semi-metal (chiral) SWNT. Image credit H. Nakahara [126].

Besides their extreme scale, one of the most striking features of SWNTs is their chirality-dependent transport. SWNTs can be modeled as graphene sheets that have been rolled up into a hollow cylinder. Depending on the chiral twist of the cylinder relative to the graphene lattice, SWNTs can exhibit both semiconductor and metallic bandstructures. Fig.
1.4 depicts three cases of different chiralities with: semiconductor (zig-zag), metal (armchair) and semi-metallic (chiral) bandstructures.

The bandstructure of SWNTs can be derived by imposing boundary conditions on the bandstructure of graphene. Fig. 1.5 is a plot of the graphene Dirac dispersion which appears as a cone in 2D momentum space [128]. For SWNTs, electronic confinement along an extra dimension allows only for states appearing as discrete 1D slices through the Dirac cone. In Fig. 1.5, depending on the chirality of the SWNT, the lowest energy band can lie at the charge neutrality point near $E_F$ (left) or further away leading to a bandgap (right). Many different types of SWNTs chiralities are possible with bandgaps that vary from 0 − 2 eV. More detailed information about SWNT bandstructure can be found in numerous review articles and books [12].

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{graphene_dirac_cone.png}
\caption{Both metallic (left) and semiconducting (right) bandstructures are visualized by taking different 1D slices through the graphene Dirac cone.}
\end{figure}

One important consequence of the Dirac dispersion is a small Fermi surface that severely constrains the phase space available for acoustic phonon scattering [3, 117]. This is unlike typical materials for which acoustic phonon scattering is often the dominant source of electronic scattering. The suppression of acoustic phonon scattering enables some SWNTs to exhibit quasi-ballistic conduction up to room temperature with an inelastic mean free path.
approaching 1 µm [147, 18, 39]. However, often other scattering mechanisms dominate the electronic resistance of SWNT devices, including SWNT optical phonons [143], substrate optical phonons [18], contact resistance [105], defects [54, 48] and disorder [49].

1.4 Low-dimensional conductors in nascent technologies

Because of their unique electronic properties, low-dimensional conductors are predicted for use in many different nascent technologies. The International Technology Roadmap For Semiconductors calls for transistor channels that will extend into the low-dimensional regime [22]. Physicists and engineers are currently looking to SWNTs as a possible alternative to the current silicon based technology due to their superior thermal conductivity and unique 1D, coaxial electrostatics [24, 157]. In another example, topological 2D systems are currently being explored for spintronics [141] and quantum computing applications [124] due to their topologically protected surface states [60]. More recently, it has been predicted that the unique optical properties of graphene and atomically thin transition metal dichalcogenides will prove useful as light emitters, detectors and energy harvesters [182]. However, despite these (and many more) predicted applications, there are significant barriers for developing low-dimensional conductors into usable technologies.

One of the largest barriers facing low-dimensional conductors is their extreme sensitivity to the surrounding environment. For the most part, the physical properties of graphene, SWNTs and the transition metal dichalcogenides are already well understood. However, as soon as one of these materials is placed into a working device these properties break down. In the non-deal environment of a working device, the presence of defects [54], disorder [19], substrates [20] and electrical contacts [105] are sufficient to alter the properties of these
materials so that their behavior is no longer well understood.

Experimentally characterizing and modeling the complex electronic transport physics of 1D conductors in working devices is a grand challenge and the primary focus of this work. The 1D case is particularly challenging compared to 2D because of the significantly lower carrier density and sensitivity to the surrounding environment. For 1D, traditional transport spectroscopy or optical characterization is often not sufficient to tease out the many different mechanisms of electronic resistance that exist simultaneously in a working device. Therefore, this work focuses on scanning probe characterization in order to spatially resolve and separate the various mechanisms of resistance in order to quantitatively study electronic scattering in 1D.
Chapter 2

Experimental Methods

2.1 SWNT field effect transistors

SWNT field effect transistor (FET) devices were manufactured on 4” Si wafers using techniques common for the field, namely chemical vapor deposition (CVD) and conventional optical lithography. Numerous recipes are available for the CVD growth of dilute, high quality SWNTs on Si wafers. Our implementation used amonodisperse nanoparticle, Fe$_{30}$Mo$_{84}$, as the catalytic seed to initiate SWNT growth. The nanoparticle seed was initially synthesized, following previous reports, as a water-soluble, ligand-terminated, icosahedral FeMo keggin molecule [125, 2]. Using an excess of the metallorganic molecules in ethanol, a saturated solution was prepared at room temperature, allowed to settle, and then decanted. A 1000:1 dilution of the saturated solution was spun onto 4” p++ Si wafers to produce a dilute but uniform coating. Oxidation in air at 700$^\circ$ C collapses the keggin molecules into catalytically active, solid particles that are suitable for growing dilute, isolated SWNTs at an areal density of approximately 0.1 $\mu$m$^2$ [2, 65].

SWNT synthesis occurred in a custom-built, 115 mm quartz tube furnace operating at 940°C. After an initial reduction of the particles in H2 (520 sccm) and Ar (3000 sccm), the addition of CH4 (1000 sccm) initiates the spontaneous nucleation and growth of SWNTs. Similar conditions in smaller furnaces have been reported to grow SWNTs with long lengths and excellent electrical characteristics [2, 65]. Our SWNTs are characterized by a combination of scanning electron microscopy (SEM, JEOL JSM-6060 at 1 kV) and by noncontact atomic force microscopy (AFM) (Pacific Nanotechnology Nano-R). SWNTs in this work fell in a diameter range of 0.9 – 1.9 nm, with process variations such as residual H2O contributing to smaller or larger SWNTs.

Figure 2.1: A cartoon of an SWNT FET (a) with corresponding plots of $I_{SD}$ versus $V_D$ (b) and $I_{SD}/I_0$ versus $V_G$ (c) for a semi-metallic (black) and semiconductor (red) SWNT. These curves were acquired under high vacuum conditions at a pressure of $10^{-7}$ Torr.

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Fig. 2.1 (a) is a cartoon of a SWNT after electrodes have been patterned down to make a FET device. After CVD, wafers were processed with optical lithography to define Ti or Ti/Pt electrodes on top of the randomly grown SWNTs. An undercut bilayer resist (S1808 on top of LOR-A1, MicroChem) was used to improve liftoff and give cleaner interfaces. The separation between source and drain electrodes was typically 2 µm, though SWNTs oriented at an angle to the electrodes produced longer channel lengths. The p++ substrate, separated from the SWNTs by a 250 nm SiO₂ thermal oxide, provided a shared back-gate electrode.

Fig. 2.1 (b) and (c) are plots of the FET electrical properties. After fabrication, automated, wafer-scale electrical characterization identified individual SWNT devices to be either semi-conducting or semi-metallic, in approximately the 2:1 ratio predicted theoretically [119, 58]. Fig. 2.1 (a) is a plot of the source-drain current $I_{SD}$ as a function of the applied drain voltage. At low bias the curve is linear but at higher bias the current begins to saturate due to carbon nanotube optical phonon scattering [185]. Fig. 2.1 (b) is a plot of the normalized source-drain current $I_{SD}/I_0$ as a function of the Si back gate potential $V_G$ for both a semi-metallic (black) and a semiconducting (red) SWNT. For the semiconductor, the Si back gate tunes the carrier density to zero at bias of $V_G = 2$ V and the current drops to zero. For the semi-metallic SWNT, a shallow dip is observed in $I_{SD}$ but the carrier density cannot be tuned to zero.

2.2 Defect incorporation by point functionalization

After initial characterization of SWNT devices in a pristine state, some devices were selected to be chemically modified to incorporate different types of defects for characterization. The general procedure, described previously as point functionalization [54, 25, 85], involves driving an electrochemical oxidation reaction between the SWNT and an electrolyte while monitoring for changes in the SWNT conductance $G$. After the initial electrochemical charging of
double layer capacitances, the covalent addition of individual defects is revealed by discrete changes in $G(t)$. This work focuses on defects produced using oxidation in DI water (18 MΩ, Nanopure), concentrated sulfuric acid (18 M H$_2$SO$_4$), or concentrated hydrochloric acid (12 M HCl).

### 2.2.1 Point functionalization

To introduce defects, a device was first coated in poly(methyl methacrylate) (PMMA A3, MicroChem) and patterned to expose a portion of the SWNT channel. This exposure window was centered at the device midpoint to spatially separate the results of point functionalization from features like Schottky barriers at either end of the SWNT channel. AFM imaging confirmed the positioning of the exposure window over each SWNT and the presence of a protective coating over the remaining majority of the surface, including the source and drain electrodes and the electrode-SWNT interfaces.

Fig. 2.2 is a cartoon depicting point functionalization of a SWNT device. Using an xyz manipulator, microtubing (0.030”) containing electrolyte was positioned over the exposed region and lowered to bring a small droplet into contact with the surface. The electrolyte potential was controlled using a Pt pseudo-reference electrode (RE) located in the droplet at the chip surface. Electrochemical modifications were controlled using a custom-built, multipotential bipotentiostat and LabVIEW software. The SWNT source, drain, and gate electrodes as well as an additional Pt counter electrode (CE), were all independently controlled with respect to the Pt pseudoreference during electrochemical modifications.

In this scheme, the exposed portion of SWNT constitutes an electrochemical working electrode, and oxidation of the SWNT was performed by biasing it at 0.9 – 1.2 V (versus Pt), depending on the oxidative threshold of each electrolyte used [54]. Simultaneously, the SWNT conductance $G$ was independently monitored by applying a source-drain potential
$V_{SD} = 0.1$ V and digitizing a transimpedance current preamplifier (Keithley 428) at 100 kHz. After oxidation had reduced $G$ below a selected threshold, each SWNT is electrochemically reduced to drive off noncovalently bound counter ions and recover a portion of the initial value.

After chemical modification, an acetone soak was used to strip the protective PMMA and expose the entire device for AFM imaging. Stable electrical behavior indicated that the PMMA removal did not affect the chemistry of the SWNT modifications. We note that a much simpler process is to perform point functionalization without any PMMA processing; but in this case, the technique preferentially creates defects within 500 nm of an electrode, which compromises subsequent scanning probe imaging.
2.2.2 Point functionalization with a software trigger

The point functionalization method described in Sec. 2.2.1 has a limited success rate for single-defect incorporation and can often introduce more extensive oxidation. The defect sites introduced by this method are discussed in Chapter 6 and the variability is discussed in detail in Sec. 6.3.5. For high-throughput incorporation of single defects, a more controlled point functionalization method is required. This section describes LabVIEW software developed for more precise control of the oxidation process to increase the success rate for single-defect incorporation.

As described in section 2.2.1, point functionalization requires monitoring the device conductance $G(t)$ for discrete steps that indicate the incorporation of individual defects. In this method, the user is required to monitor these discrete drops and halt the oxidation process manually. However, at the threshold for oxidation, defects are typically added at a rate of one per $\approx 100$ ms [54] and often the user is not able to respond quickly enough to halt the process after only a single drop in $G(t)$.

To overcome this problem, a software trigger was developed to halt the oxidation process automatically after the incorporation of a single defect. Fig. 2.3 is a screenshot of the software user interface for electrochemical point functionalization and triggering. Using the Ke4200 control panel, the user ramps the liquid to a target potential in small voltage steps while monitoring the device conductance. At the potential threshold for oxidation, the user arms the software trigger using the control panel outlined in light blue. When the trigger has been activated due defect incorporation the liquid is sent to the jump potential selected in the Ke2400 control panel.

Fig. 2.4 is a plot depicting single-defect incorporation using the software trigger. During the oxidation process the device conductance $G(t)$ (black dots) was acquired at a rate of 100 kHz in 25 ms buffers and plotted vs the reference electrode potential RE (red line). Here, $G(t)$
Figure 2.3: A LabVIEW program controls the electrochemical oxidation process for point functionalization.

maintained a constant value of 3.75 $\mu$S at the threshold for oxidation $RE = -1.0$ V until a discrete drop was observed at $t = 300$ ms corresponding to single-defect incorporation.

The software trigger calculates the average value of the conductance $G_{avg}$ in each 25 ms buffer of $G(t)$ data. The trigger buffer (highlighted in black along the time axis) is compared to a moving average $G_{m,avg}$ of the last ten buffers (highlighted in yellow). The trigger threshold condition $G_{avg}/G_{m,avg} < 0.85$ is sensitive to the discrete steps in $G(t)$ corresponding to defect incorporation. If the condition is met, the trigger automatically sends the liquid to a neutral
Figure 2.4: The device conductance $G(t)$ and liquid potential $RE(t)$ (red line) are plotted during single defect incorporation using a software trigger.

potential of $-0.3 \text{ V vs Pt}$ to halt the oxidation process. In some cases, such as in Fig. 2.4, the liquid potential was sent directly to 0.5 V in order to immediately reduce the defect chemistry.

There is a short delay of $5 - 10 \text{ ms}$ that occurs between when the threshold condition is met and the liquid potential is sent to the jump value. The delay, highlighted in red in Fig. 2.4, is due to the fact that the calculation of the threshold condition and corresponding response are carried out using a parallel processor on a PC. This delay limits the response time of the software trigger to $30 - 35 \text{ ms}$, but is short enough that the trigger responds to halt oxidation after single-defect incorporation in greater than $80\%$ of attempts. It should be noted that the use of a field programmable gate array for triggering would overcome the delays due to parallel processing and further reduce the trigger response time.

2.3 Atomic force microscopy with a JEOL JSPM-5200

Both pristine and defective SWNT FET were characterized in a high-vacuum, variable temperature JEOL JSPM-5200 atomic force microscope (AFM) at $10^{-7} \text{ Torr}$ and $130 - 300 \text{ K.}$
The JSPM-5200 was used to investigate the electronic properties of the FET *in operando* using both scanning gate microscopy (SGM) and Kelvin probe force microscopy (KPFM) imaging modes. The device source, drain, and backgate potentials ($V_S$, $V_D$, and $V_G$, respectively) were each controlled by custom software that integrated external analog signals (National Instruments NI-6289) into the device. Imaging was carried out with conventional silicon cantilevers (MikroMasch ULTRASHARP NSC15) coated with a 10 nm Pt film with a probe tip radius of curvature $r = 30 – 40$ nm. The SGM and KPFM imaging techniques are introduced in Sec. 2.3.2 and Sec. 2.3.1, respectively.

### 2.3.1 Kelvin probe force microscopy

Kelvin probe force microscopy (KPFM) is a technique for measuring the local work function $\Phi$ of a sample surface using a conductive AFM probe. The work function contains information about the sample electrochemical potential and surface chemistry that are critical for the function of nanoscale transistors. In KPFM, $\Phi$ is determined relative to the probe work function $\Phi_0$ by measuring the contact potential difference $\Phi_{KP} = \Phi - \Phi_0$ using a method similar to Lord Kelvin in 1898 [88].

In Fig. 2.5 a metallic probe capacitively couples to the sample surface. To determine $\Phi_{KP}$, KPFM relies on measuring the electrostatic force $F_{el}(z)$, or force gradient $\partial F_{el}/\partial z$ between the probe tip and the sample surface. The force gradient is simply

$$\frac{\partial F_{el}}{\partial z} = \frac{1}{2} \frac{\partial^2 C}{\partial z^2} (V_{KP} - \Phi_{KP})^2$$

(2.1)

where $C$ is the capacitance between the probe and the sample surface and $V_{KP}$ is the voltage applied to the tip. In practice, $\Phi_{KP}$ is determined by applying $V_{KP}$ so that $\partial F_{el}/\partial z = 0$. 
Figure 2.5: A schematic of Kelvin probe force microscopy of nanoscale FET *in operando*. The probe tip is used to measure the force due to the local contact potential difference by capacitively coupling to the transistor surface.

This is either carried out using force spectroscopy, where the $V_{KP}$ is ramped to find a force minimum, or by implementing a feedback loop that actively sets $\partial F_{el}/\partial z = 0$. Force spectroscopy is typically carried out when investigating potential distributions that approach the atomic scale and requires many hours of measurement time [57]. For this work, a feedback loop was implemented to increase the measurement speed.

When a Kelvin feedback loop is implemented, a small AC bias $V_{AC}$ must be applied to the tip in order to distinguish $F_{el}(z)$ from the vdW force and other chemical forces such as Pauli repulsion [30]. By effectively distinguishing between the electrostatic and vdW force, the topography and work function of the surface can be imaged simultaneously. Making the
substitution of $V_{KP} = V_{DC} + V_{AC}\sin(\omega t)$ into Eq. 2.1 yields

\[
\frac{\partial F_{el}}{\partial z} = \frac{1}{2} \frac{\partial^2 C}{\partial z^2} [(V_{DC} - \Phi_{KP})^2 + \frac{1}{2} V_{AC}^2] \\
\frac{\partial^2 C}{\partial z^2} (V_{DC} - \Phi_{KP}) V_{AC} \sin(\omega t) \\
\frac{1}{4} \frac{\partial^2 C}{\partial z^2} V_{AC}^2 \cos(2\omega t).
\]  

(2.2)

In Kelvin feedback, a lock-in amplifier is used to demodulate the first harmonic term proportional to $V_{AC}\sin(\omega t)$ which is used as an error signal for the Kelvin feedback loop. Further details of the KPFM signal processing and the experimental characterization of FETs are described in Chapter 3 and Chapter 4, respectively.

In the strictest terms, $\Phi$ is defined as the energy difference between two states of a semi-infinite solid metal at $T = 0$ K [99]. The energy differences are shown as a schematic in Fig. 2.6 (b). In one state, an electron exists at the Fermi level within the solid and in the other state the electron has been ionized and exists infinitely far from the solid surface. Conceptually, this energy difference is explained as the chemical potential energy required to remove an electron at the Fermi level $\bar{\mu}$ with an additional term due to the change in potential energy required for the electron to cross the dipole layer at the solid surface $\Delta \phi$. In total, this yields $\Phi = \Delta \phi - \bar{\mu}$.

The macroscopic concept of a semi-infinite solid must be modified in order to discuss local variations in $\Phi$ that exist at the nanometer scale. For real surfaces that are found experimentally, the sample has finite dimensions, is made of discrete atoms and includes chemical and structural disorder. These considerations lead to the concept of a local surface term $\Delta \phi(x, y)$, due to local variations in the surface charge distribution from chemical and structural disorder [179]. The concept of the local work function can be extended to the nanometer scale but
begins to break down at the scale of individual atoms [123]. Here, KPFM can yield atomic scale contrast related to individual surface charges, but the exact origin of the contrast is currently being worked out for different surfaces [57, 157].

While the term $\Delta \phi(x, y)$ is related to surface charges, the electrochemical potential $\bar{\mu}$ is related to electronic transport. In the macroscopic view of work function, $\bar{\mu}$ is the bulk chemical potential of electrons with respect to the electrostatic potential of the solid [99]. However, in a nanoscale transistor, changes in the local electrochemical potential $\mu(x, y)$ occur under non equilibrium, steady-state current flow. These changes are due to the inelastic electronic scattering that gives rise to localized electronic resistance [17, 29, 107]. Together,
variations in the local surface charge and electrochemical potential give rise to a local contact potential difference $\Phi_{KP}(x,y) = \Delta\phi(x,y) - \mu(x,y) - \Phi_0$ that contains information about the local surface chemistry and the underlying electronic transport. For transistors, each term is critical as surface chemistry strongly influences the electronic transport of the underlying transistor channel [27].

2.3.2 Scanning gate microscopy

Scanning gate microscopy (SGM) is a technique that uses a conductive AFM probe as a moveable source of electric field in order to tune the local carrier density within an electronic circuit [84]. An SGM image produces a map of the device conductance in response to the probe position $G(x,y)$ that indicates the location of a circuit’s sensitivity to electric fields. For low-dimensional materials the influence of the AFM probe can constrict the current flow substantially and in the extreme case of a one-dimensional conductor, the current flow can be constricted to zero [69].

Fig 2.7 is a schematic of the SGM technique. Here, a bias $V_{AC}$ is applied to the drain electrode and the corresponding current is measured using a transimpedance amplifier. The amplifier output signal is sent to a lock-in amplifier for low-noise demodulation of the device conductance $G(x,y)$. SGM and its applications to SWNT FETs are described in detail in Chapter 6.
Figure 2.7: A schematic of scanning gate microscopy of a working FET.
Chapter 3

High-speed Kelvin probe force microscopy for electronic transport spectroscopy

3.1 Introduction

Electronic transport spectroscopy of nanoscale transistors is a technique for studying the quantized energy states that dominate their electronic properties [109]. When transport spectroscopy is combined with spatially resolved electronic information from Kelvin probe force microscopy (KPFM) the location and origin of these states is revealed. The powerful combination of energetically and spatially resolved information motivates the extension of KPFM into a transport spectroscopy. However, transport spectroscopy requires measuring the device current $I_{SD}$ while sweeping the source-drain bias $V_{SD}$ and gate bias $V_G$ over a wide range of voltages. For KPFM, this requires many sets of images taken at many discrete points in the $I_{SD}(V_{SD}, V_G)$ parameter space. The notoriously slow imaging speed of KPFM
combined with the large number of images required often leads to 24 hours or more of measurement time [123]. For many applications, various experimental conditions prevent such extended measurement times and KPFM transport spectroscopy is not an accessible research tool.

Despite the lengthy measurement times reported in the literature, the relatively slow imaging speed of KPFM is often due to the corresponding instrument electronics as opposed to more fundamental physical limitations. These limitations arise from the fact that for a typical scanning probe microscope the KPFM signal processing electronics are shared with other primary imaging modes (i.e. the sample surface topography) and this has the effect of dramatically slowing the overall measurement speed. Fortunately, there are now several commercial products that provide dedicated signal processing electronics for KPFM, including the Nanonis Oscillation Controller OC4 and the Zurich Instruments HF2LI lock-in amplifier. These products can be interfaced with an existing scanning probe microscope to successfully implement KPFM feedback while maintaining typical AFM imaging speeds.

This chapter describes modifications to a JEOL JSPM-5200 scanning probe microscope for KPFM transport spectroscopy. Sec. 3.2 describes interfacing the JSPM-5200 with a Zurich Instruments HF2LI lock-in amplifier for high-speed KPFM. Sec. 3.3, describes the installation of a low-noise amplifier for an improved signal to noise ratio during high-speed KPFM. Sec. 3.4 describes the implementation of scan control software for automating the acquisition of spectroscopic data sets. Finally, Sec. 3.5 summarizes the modifications to the instrument and demonstrates its utility in carrying out transport spectroscopy.
3.2 Digital signal processing and feedback control with a Zurich Instruments HF2LI

For typical KPFM, a phased locked loop (PLL) is used to track shifts in a probe cantilever resonance frequency due to both the surface topography and surface potential signals. The surface topography is a slowly varying signal with frequency components that are less than 1 kHz while the surface potential is measured by tracking a higher frequency signal > 1 kHz. Because the topography and surface potential signals are tracked with a single PLL, a conflict arises when sharing the PLL bandwidth. Typical PLL bandwidths are limited to only a few kHz and the spread in frequency between the two signals results in a restricted KPFM bandwidth and slow imaging speeds.

The JEOL JSPM-5200 scanning probe microscope has a single PLL used for tracking both the surface topography and surface potential signals. Fig. 3.1 is a power spectrum of the JSPM-5200 cantilever deflection signal about the cantilever resonance frequency at \( f_0 = 77 \) kHz. The dominant peak at \( f - f_0 = 0 \) Hz is the topography signal from the cantilever oscillation on resonance due to mechanical excitation. The peaks directly to the left and right of resonance are the surface potential signals due to the KPFM excitation at 2 kHz. For KPFM imaging with a single PLL, the bandwidth must envelope both topography signal at \( f - f_0 = 0 \) Hz and the surface potential sidebands at +2 and -2 kHz as highlighted in red in Fig. 3.1. Since typical PLL bandwidths do not extend past a few kHz at most, the resulting KPFM bandwidth is often restricted to of 200 – 400 Hz.

In contrast to a single PLL, an HF2LI uses multiple PLLs to track each signal as highlighted in green in Fig. 3.1. Here, three separate PLLs track both the surface topography signal near resonance and the two surface potential sidebands at +2 and -2 kHz. The PLL bandwidths can be individually optimized for both topography and surface potential imaging and as a result the KPFM feedback is no longer restricted by the limited bandwidth of a single PLL.
Figure 3.1: A power spectrum of the topography and surface potential signals about the cantilever resonance frequency.

Additionally, because both sidebands are tracked independently, they can be added in such a way to double the overall surface potential signal and increase the overall signal to noise ratio. The end result is a higher bandwidth KPFM feedback with a higher signal to noise ratio and KPFM imaging at typical AFM imaging speeds.

Fig 3.2 is a schematic of the interface between the HF2LI and the JSPM-5200 for KPFM signal processing and feedback control. The cantilever deflection signal (to be described in in Sec. 3.3) enters at Input 1 where it is digitized and then processed by various modules to track the surface topography and surface potential signals. The topography signal processing and feedback control are visualized by following the flow of information between PLL1 and PID3 in Fig. 3.2. The shift in the cantilever oscillation frequency due to topography (labeled f topo) is tracked by PLL1 using OSC1. The frequency is then sent to PID3 where it is used as an error signal for the topography feedback loop. The output of PID3 is sent to the SPM controller via Aux 4 to control the probe-sample distance.
Figure 3.2: A schematic showing the flow of information between the different processing components inside the HF2LI during KPFM feedback. The topography (KPFM) feedback loop has been highlighted red (green).

The surface potential signal processing and Kelvin feedback control are visualized by following the flow of information between Input 1, MOD1 and PID4 in Fig. 3.2. The cantilever deflection signal is sent directly to MOD1 to measure the surface potential signal. MOD1 utilizes PLL2 and PLL3 to demodulate the surface potential sidebands at the KPFM excitation frequency $+f_{KPFM}$ and $-f_{KPFM}$ respectively. The output of PLL2 and PLL3 are then sent to PID4 where they are combined as an error signal for the Kelvin feedback loop. The output of PID 4 (labeled CPD) is sent to Output 2 to be recorded by an NI-6289 multifunction data acquisition board. Output 2 is also added to the DC potential of the probe tip using the Add 2 channel.

Using the HF2LI to track the topography and surface potential signals with multiple PLLs
increased the maximum imaging speed of the JSPM-5200 from 500 nm/s to almost 2.5 \( \mu \text{m/s} \). The increase in speed dropped the time for acquiring 75 images with a 2 x 2 \( \mu \text{m} \) scan area from 21 to 4 hours. This improvement in speed allowed for electronic devices to be studied over a wider variety of conditions in reasonable time frames.

3.3 Optical beam deflection and analog signal processing with a low-noise amplifier

In KPFM, the bandwidth of the Kelvin feedback loop determines both the maximum imaging speed and the amount of rejected noise. There is a trade-off between raising the bandwidth to decrease the feedback response time and a corresponding decrease in the amount of rejected noise. For high-speed imaging it is critical that instrument noise is carefully eliminated from the experimental setup in order to achieve an acceptable signal to noise ratio at high bandwidth. For the JSPM-5200, the noise entering into the Kelvin feedback loop is dominated by extrinsic sources arising in the instrument electronics rather than intrinsic sources such as the probe or the sample surface. This section describes the noise performance of the original JSPM-5200 amplifier electronics and the design of a new low-noise amplifier for higher speed KPFM.

The JSPM-5200 uses the optical beam deflection (OBD) method for measuring the electrostatic force that is used for feedback. OBD from a probe cantilever is one of the most popular and simplistic methods for detecting forces between an AFM probe and a sample surface [118]. However, despite the popularity of OBD, noise from the deflection sensor can severely limit the sensitivity of the instrument [1] and OBD is typically inferior to interferometer based detection [46].

Fig. 3.3 depicts the OBD method of detecting force acting on a probe cantilever. The
z-component of the force is determined by the cantilever displacement $\Delta z$ and the spring constant $k$ through the relationship $F_z = k\Delta z$. The displacement $\Delta z$ is detected by reflection of a laser from the end of the cantilever to a position-sensitive photodetector (PSPD). The displacement $\Delta z$ gives rise to a change in position of the laser spot on the PSPD by an amount $\Delta a = 3(s/l)\Delta z$, where $l$ is the cantilever length and $s$ is the distance from laser spot to the PSPD [155]. For the JSPM-5200 dimensions and typical cantilever lengths ($\approx 100\mu m$) this gives rise to about a $10^3$ amplification.

Figure 3.3: Optical beam deflection in the JEOL JSPM-5200 microscope. Reprinted from [47]. ©American Institute of Physics

Noise can enter into the OBD sensor from the cantilever, the laser diode or the PSPD. The noise resulting from Brownian motion of the cantilever is the physical limit to the force sensitivity. However, Brownian noise is often negligible compared to noise introduced by the PSPD and laser. Typically, the PSPD introduces substantial photodiode shot noise and the laser introduces noise through the mechanisms of laser mode hopping and optical feedback. Each of these sources of noise can be reduced by careful design of the corresponding OBD electronics and the sensor can be optimized to compete with interferometer based detection to exhibit Brownian limited noise performance [46].

In most well-designed OBD sensors, shot noise is the predominant source of noise introduced by the PSPD. The shot noise scales inversely to the incident laser power and the power can
be increased to reduce the overall sensor noise. Fig. 3.4 is a plot of the deflection noise density of a cantilever in the JSPM-5200 as a function of laser power (red dots). The dashed curve is a plot of the theoretically calculated shot noise. At low laser power the measured noise is well-fit to the calculation, but at a laser power above 2.5 mW the noise increases again due to mode-hop noise.

![Figure 3.4: The deflection noise for a cantilever as a function of laser power in the JEOL JSPM-5200 microscope (red dots). The theoretically calculated deflection noise due to photo diode shot noise is shown as a dashed line. Reprinted from [47]. ©American Institute of Physics](image)

At low power a laser is inherently multi mode with a relatively broad frequency spectrum and introduces very little noise to the PSPD. Mode hop noise occurs when the laser power is increased to the point that the laser operates at a single mode. During single mode operation the laser has a tendency to spontaneously hop between competing modes. Even though the modes are closely spaced in energy, this spontaneous hopping causes strong fluctuations in the laser intensity at the PSPD and introduces a significant amount of noise into the OBD sensor.

Another closely related source of noise is induced by optical feedback and optical interference, herein called "optical interference noise" [130]. In the optical system in Fig. 3.3 some of the laser light can be reflected back to the laser diode where it induces mode hopping, even at
low power. Additionally, laser interference introduces broadband intensity fluctuations at
the PSPD. Optical interference noise depends sensitively on the distance of the optical path
between the laser cavity or PSPD and a reflective surface. Small changes in temperature and
sample position can bring the reflected light in and out of interference. Therefore, optical
interference noise tends to wander in and out of the OBD system on the scale of hours as
the laser case expands and contracts due to thermal drift.

To reduce the overall deflection noise in the JSPM-5200 OBD system the laser power must
be increased to reduce the PSPD shot noise but not beyond the threshold for hop mode noise
identified in Fig. 3.4. Destroying the laser coherence also helps to to prevent additional noise
from optical interference. A new amplifier based upon the design by Fukuma et al. [47] was
installed to reduce these sources of noise, replacing the standard JSPM-5200 electronics.

A schematic of the new amplifier shown is shown in Fig. 3.5. The amplifier consists of three
main components: the photodiode signal processing (PSP) board, the laser diode driver
board and a voltage controlled oscillator (VCO). The PSP board amplifies and processes the
laser deflection signal from the cantilever before sending it to a controller for digital signal
processing and feedback control. The laser driver (Thorlabs IP500) drives the output of the
laser to high power to reduce photodiode shot noise. The VCO modulates the laser power
at RF frequencies to force the laser into multi mode operation (even at high power) and
destroy the laser coherence in order to lower the optical interference noise [47].

Fig 3.6 is a plot of the laser output specifications for the Hitachi HL6714G laser diode used
in the JSPM-5200. In Fig 3.6 (a), the laser power is shown to have a threshold at a forward
current of roughly 35 mA, beyond which the power increases steeply. In ideal conditions, a
constant forward current will deliver a constant laser output. However, the current threshold
is highly temperature dependent and small changes in laser temperature will cause the output
to drift. Therefore, a feedback mechanism must be employed to counteract drift and maintain
a constant laser power.
Figure 3.5: An electronic schematic of the new amplifier installed into the JEOL JSPM-5200 microscope.

Fig. 3.6 (b) is a plot of the optical output power as a function of monitor photodiode current for the HL6714G. The laser monitor photodiode (integrated directly into the laser diode chip) directly monitors the output power of the laser. The monitor photodiode current can be used for feedback to regulate the laser diode forward current and accurately control the laser power independent of thermal drift. The plot in Fig. 3.6 (b) can be used in conjunction with a laser driver to precisely tune the laser to desired power.

The IP500 laser driver was chosen because it can operate at higher power than the original JSPM-5200 laser driver and can utilize a variety of feedback modes. In the configuration shown in Fig. 3.5, the IP500 drives the laser using an automatic constant power control (APC) feedback loop. In APC feedback, the monitor photodiode current is used by the IP500 PID controller to regulate the laser power. The monitor photodiode current (labeled
Figure 3.6: The power output for specifications for a Hitachi HL6714G laser diode.

PD) enters the amplifier from connector FA1 where it then connects into the IP500 at connector J2. The IP500 sources the laser forward current through LD where it returns along COM. A desired laser output is set by adjusting the monitor photodiode current set point using a trim pot resistor located on the IP500 circuit board.

In Fig 3.5 the DC output of the laser is controlled by the IP500, but an additional RF modulation is added to the laser forward current by a Mini-Circuits ZX95-400+ voltage controlled oscillator in conjunction with a Thorlabs T1G RF bias-tee. The RF power (10 dBm at 200 MHz) delivered to the laser has the effect of destroying the laser coherence and reducing noise due to optical interference. The RF modulation frequency is tuned via a trim pot resistor located on the front of the amplifier box. However, the precise frequency of the RF modulation is not important so long as it is far from the cantilever oscillation frequency so as to prevent crosstalk with the cantilever deflection signal.

In Fig. 3.5, the signals entering the PSP board \( a_1, a_2, b_1, \) and \( b_2 \) are proportional to the four-segment Si PIN photodiode (Moririca MI-33H-4D) currents from the PSPD. The signals \( a_1 \) and \( a_2 \) correspond to the top two segments while the signals \( b_1 \) and \( b_2 \) correspond to the
bottom segments. A vertical probe movement $\Delta z > 0$ corresponds to changes in the laser spot $\Delta a > 0$ at the PSPD resulting in increased signal at $a_1$ and $a_2$ and decreased signal at $b_1$ and $b_2$. The first stage of the PSP electronics combines the signals to create $A = a_1 + a_2$ and $B = b_1 + b_2$ using two adders. The second stage creates the signal $A - B$ which is proportional to the cantilever displacement. In the final stage, the cantilever deflection signal (AFM) is created by the division $(A - B)/(A + B)$. The division creates a deflection signal with a magnitude that is relatively independent of the laser power incident to the PSPD. This is useful for preventing signal drift to small DC changes in the laser power and to ensure cantilevers with different reflectivities give a similar amplitudes. However, the signals $A - B$ and $(A - B)/(A + B)$ are both proportional to the cantilever deflection $\Delta z$, have similar signal-to-noise ratios and in most cases can be used equally well for imaging.

Fig 3.7 shows a power spectra of the cantilever deflection signal to summarize the differences between the original and the new amplifier. For each spectrum, the deflection signal appears as a peak around 250 - 300 kHz, at the resonance frequency of an AFM cantilever. For this plot, several cantilevers were used with slightly different resonant peaks and amplitudes of oscillation. Since the new amplifier has identical gain to the original, the absolute frequency or magnitude of the OBD signal is not important. Instead, the important aspects are the reduced noise baseline about the resonance peak in order to increase the overall signal to noise ratio.

The original amplifier noise baseline was at -85 dB at a laser power of 0.5 mW. This noise baseline wandered between -80 to -90 dB from hour to hour depending on the amount of optical interference noise caused by reflection from the tip or sample surface. At the same laser power of 0.5 mW, the new amplifier box performed almost identically because the dominant noise sources were photo diode shot noise and optical interference. As demonstrated in Fig 3.4, tuning the IP500 to output 2 mW of laser power dropped the noise baseline dramatically to -97 dB as it minimized the photo diode shot noise. However, this baseline
was found to wander between -90 to 100 dB due to optical interference. Finally, turning on the RF modulation by the VCO results in a stable noise baseline of -100 dB as it forces the laser into multi mode operation and reduces optical interference noise. A reduction of 10-15 dB greatly improved the signal-to-noise ratio especially at the sidebands (Fig. 3.7) that are critical to KPFM imaging.

3.4 Automated scan control with National Instruments NI-6289

For KPFM transport spectroscopy of nanoscale transistors, images must be acquired at many different values of source-drain and gate bias. For large sets of images, an auto-
mated approach to scanning is preferred over manual control. The image dimensions are also an important consideration as they contribute to the overall measurement time. The standard image for commercial scan software is square, but for many nanoscale devices the geometry of interest is rectangular. In particular, single-walled carbon nanotubes and other one-dimensional channels represent an extreme case with aspect ratios approaching 1000:1. Acquiring square images costs extra time and produces extraneous information. This inefficiency is especially problematic for spectroscopy because the added time is multiplied by the large number of images. These considerations motivate the development of custom software to automate scanning at different device biases and to adjust the image shape to reduce the overall measurement time.

Custom LabVIEW software was written to automate scanning and to create custom images using the JSPM-5200. The scan software works by controlling the JPSM-5200 lateral piezo motion with voltages from a National Instruments NI-6289 multifunction data acquisition board. The voltages are sent to the ADX and ADY ports on the JSPM-5200 Controller, which allow for external control of the x and y piezo motion respectively. The LabVIEW software also synchronizes data acquisition with scanning by acquiring the various signals of interest using the NI-6289 analog inputs.

Fig. 3.8-3.9 is a snapshot of the user control panel for KPFM transport spectroscopy using the custom LabVIEW software. In Fig. 3.8 the user selects custom image shape within a square scan area. Only the pixels encapsulated by the area highlighted in green will be scanned during imaging to reduce the measurement time.

In the next control panel shown in Fig. 3.9, the user automates scanning multiple images at various source-drain and gate voltages. Here, the main loop controls the source-drain bias through the NI-6289 analog output AO0, while the nested loop controls the gate bias through output AO1. After the user selects the desired biases, scanning is carried out sequentially at every bias for the first scan line within the highlighted area. When the bias sequence is
Figure 3.8: LabVIEW software allows the user to define a custom, rectangular scan area with a different aspect ratio and angle than a typical square image.

Once complete, the software moves on to the next scan line until the highlighted area has been completely imaged. Other automated scanning modes were programmed to include image by image biasing as opposed to line by line. However, the line by line mode was found to be most convenient when correcting for sample drift using image post-processing.

The custom LabVIEW software allows the user to carry out automated KPFM transport spectroscopy with a significant reduction in the scan time. The highlighted area in Fig. 3.8 contains only 30% of the of the square scan area and leads to a 70% reduction in the overall imaging time. For a single-walled carbon nanotube, the scan area could be reduced further, but acquiring additional data from the surrounding substrate turns out to be key to quantitative interpretation as will be discussed in Chapter 4.
3.5 Conclusion

An overview of the modifications to the JSPM-5200 for KPFM transport spectroscopy are highlighted in green in Fig. 3.10. The use of the controller for signal processing, scan control and data acquisition has been abandoned and it is now used only for high-voltage amplification of the piezo signals and for the stage motor control. The existing external amplifier was replaced with a new low-noise amplifier (Sec. 3.3) and the instrument has been interfaced with a Zurich Instruments HF2LI Lock-in amplifier for digital signal processing and feedback control (Sec. 3.2).

The modifications to the JSPM-5200 increased the KPFM imaging speed from 500 nm/s to nearly 2.5 μm/s due dedicated KPFM signal processing by the HF2LI. The increased
Figure 3.10: A schematic of the JSPM-5200 electronics after modification for KPFM transport spectroscopy. The added components are highlighted in green. The cable interconnects between each of the components are labeled (rectangles) so that the schematic can be used as a guide for assembling the instrument. For each of the instrument cables (dashed lines) the primary type of routed signal has been labeled. The topography feedback loop has been highlighted in blue to indicate the basic operation of the instrument. A schematic of the original JSPM-5200 electronics can be found in Appendix A.

Bandwidth required for high-speed did not come at a significant cost to the KPFM voltage noise as the new amplifier electronics have dropped the deflection noise density by 10-15 dB. In addition, the imaging time has been reduced significantly for high-aspect ratio sample geometries due to the control of image shape enabled by custom scan software. The result is an order of magnitude decrease in the imaging time for spectroscopic type data sets. Measurements that might require 24 hours or more can now be completed in just a few hours making KPFM transport spectroscopy a far more accessible research tool.
Chapter 4

Quantitative Kelvin probe force microscopy of current carrying devices

Kelvin probe force microscopy (KPFM) should be a key tool for characterizing the device physics of nanoscale electronics because it can directly image electrostatic potentials. In practice, though, distant connective electrodes interfere with accurate KPFM potential measurements and compromise its applicability. A parameterized KPFM technique described here determines these influences empirically during imaging, so that accurate potential profiles can be deduced from arbitrary device geometries without additional modeling. The technique is demonstrated on current-carrying single-walled carbon nanotubes (SWNTs), directly resolving average resistances per unit length of 70 kΩ/µm in semimetallic SWNTs and 200 kΩ/µm in semiconducting SWNTs.¹

4.1 Background

Kelvin probe force microscopy (KPFM) [151] measures surface potentials with nearly atomic resolution [92, 156] and minimal sample perturbation. Therefore, KPFM should be an ideal tool for characterizing nanoscale electronic devices, especially in cases where the device physics of novel materials is poorly understood. However, a primary limitation of KPFM is long-range capacitive coupling between the scanning probe and distant regions of a surface [151, 75, 148, 189]. This coupling allows large, distant electrodes to contribute to the potentials and potential gradients measured by KPFM and ascribed to the probe tips location. This problem is particularly acute when probing low-carrier density semiconductors, oxides, or other nanomaterials. Historically, this capacitive coupling problem has limited most KPFM research to the measurement of contact potential differences, such as work function variations between dissimilar materials [75] or across $p$-$n$ junctions [148]. Effective solutions to the coupling problem, on the other hand, would improve quantitative imaging so that KPFM could map potential distributions along current-carrying pathways in active devices. This goal is a most promising application for KPFM, since it would help determine the device physics of novel or nanostructured electronic materials like organic polymers, graphene, or silicon nanowires [75, 64].

Achieving this aim motivates the development of KPFM techniques that minimize the artifacts introduced by long-range electrostatic coupling. Experimentally, KPFM imaging can be improved by decreasing the time-averaged height of the oscillating probe cantilever [189] and by operating in a frequency-modulated mode (FM-KPFM). Both techniques help minimize the contributions from parasitic capacitances but cannot eliminate them. A mathematical consideration of the Kelvin probe potential $\Phi_{KP}(x, y)$, which for FM-KPFM is given by the
weighted sum,

\[ \Phi_{KP}(x, y) = \sum_{i=1}^{n} \alpha_i(x, y)V_i = \sum_{i=1}^{n} \frac{\partial^2 C_i/\partial z^2}{\sum_{j=1}^{n} \partial^2 C_j/\partial z^2} V_i, \]  

(4.1)

shows that every equipotential surface \( V_i \) influences \( \Phi_{KP} \) through its mutual capacitance \( C_i \) to the probe. In ideal cases, the coupling of the probe to distant surfaces is insensitive to the probes oscillation, so that \( \partial^2 C_i/\partial z^2 = 0 \) for each term except the surface potential \( V_{surface} \) immediately below the probe tip. In that special case, \( \alpha_{surface} = 1 \) and \( \Phi_{KP} = V_{surface} \). More generally, other coupling coefficients \( \alpha_i \) are nonzero, and \( \Phi_{KP} \) is a weighted average of \( V_{surface} \) and other potentials \( V_i \) interacting with the probe tip.

The KPFM literature includes many discussions of this problem, including the development of analytical and numerical models for calculating the relevant \( \alpha_i(x, y) \) and reconstructing \( V_{surface} \) from \( \Phi_{KP} \). The combination of experimental data with electrostatic modeling can be very effective in simple geometries like semi-infinite p-n junctions. This reconstruction is less effective in dense device layouts or wherever thin, semiconducting channels are biased by high-carrier-density electrodes. In those cases, \( \alpha_i \) of the electrodes can be comparable to \( \alpha_{surface} \) at distances of several hundred nm. The spatial variation of \( \alpha_i \) compounds the problem, adding voltage artifacts and preventing quantitative surface potential measurements along a path of interest. Furthermore, it is very difficult for modeling to account for surface traps, channel defects, and other device imperfections that sometimes play major roles in the performance of nanoscale devices.
4.2 Parameterized Kelvin probe force microscopy

Here, we combine the best experimental practices with an additional, empirical technique that further eliminates interference from multiple connected electrodes, so that additional modeling is not required to correctly determine potential gradients in an active, biased device. The technique involves acquiring FM-KPFM images while sweeping each relevant $V_i$ through small ranges at every pixel of interest. A semi-automated sequence of biases applied to source, drain, and/or gate electrodes generated slices of a multidimensional FM-KPFM image $\Phi_{KP}(x, y, V_i)$. Gradients $\partial \Phi_{KP}/\partial V_i$ in the data set effectively measure each $\alpha_i(x, y)$ and directly determine the spatially-dependent, relative coupling capacitance between each electrode and the KPFM probe at each pixel.

By determining $\alpha_i(x, y)$ over the entire surface, this technique parameterizes complex device geometries and allows for the separation and quantification of electrode potentials contributing to $\Phi_{KP}$ (though it does not directly improve other aspects of imaging such as lateral resolution). By comparison, modeling $\alpha_i(x, y)$ in a tool such as COMSOL Multiphysics proved too resource-intensive for general use, especially since accurate models required movement of the probe relative to the surface at each pixel. Furthermore, the experimental technique automatically accounted for device defects and strongly-interacting surface traps that could not be predicted $a priori$.

4.3 Experimental Setup

To demonstrate the technique, we examined potential gradients along individual, current-carrying, single-walled carbon nanotubes (SWNTs) in three-terminal, field effect transistor (FET) geometries. SWNT devices are an excellent test case that have proven to be quite complex in past research [15, 121, 9, 181, 41, 82, 83, 42, 73, 74]. Because of their extremely
small diameters (1 nm) and low carrier densities (1-100 \( \mu \text{m}^{-1} \)), SWNT channels couple very weakly to KPFM probe tips and some researchers have concluded that SWNT potential gradients are too small to image reliably [121, 9, 73]. Devices were mounted in a high-vacuum, cryogenic KPFM (JEOL JSPM-5200) and characterized at 10\(^{-7}\) Torr and 200 K to eliminate artifacts from the ambient environment [69, 68].

### 4.4 Results

Multiple SWNT FETs were imaged under various bias conditions, with similar results from all defect-free SWNTs. To best demonstrate the method, Figures 4.2, 4.3, and 4.4 all depict data from a single SWNT device, a semimetallic SWNT having a diameter of 1.1 nm, a channel length of 2.1 \( \mu \text{m} \), and a DC resistance of 370 k\(\Omega\). Fig. 4.2(a) shows topography and raw FM-KPFM surface potential measurements for three bias conditions. At every pixel, \( \Phi_{KP} \) was measured for a small range of biases around \( V_G = -1 \text{ V} \) and \( V_S = 0 \text{ V} \) to determine \( \alpha_G(x,y) \) and \( \alpha_S(x,y) \), respectively. Similar variation of \( V_D \) occurred around \( V_D \) set points ranging from -1.5 to +1.5 V. From slices in the multidimensional data \( \Phi_{KP}(x,y,V_i) \), the
derivatives $\alpha_G(x, y) = \partial \Phi_{KP}/\partial V_G$ and $\alpha_D(x, y) = \partial \Phi_{KP}/\partial V_D$ were determined over the entire surface.

Figure 4.2: (a) Topography (leftmost) and $\Phi_{KP}(x, y)$ for a SWNT device at three $V_D$ biases, with $\Phi_{KP}$ depicted using a color scale. (b) Simultaneously measured weighting coefficients $\alpha$ for the backgate, drain and source electrodes, and SWNT channel. (c) Line cuts of $\alpha(x)$ following the SWNT channel ($0 > x > 2.1 \ \mu m$) and extending over source and drain electrode regions. A numerical sum of the $\alpha_i$ is also shown. Dashed lines indicate approximations in regions where the technique cannot fully separate $\alpha_{SWNT}$ from $\alpha_D$ or $\alpha_S$.

Fig. 4.2(b) shows images of each $\alpha_i(x, y)$. Over the bare oxide, the probe coupled strongly
Figure 4.3: (a) Line cuts of $\Phi_{KP}(x)$ taken directly over the SWNT at ten $V_D$ biases. (b) The component of $\Phi_{KP}(x)$ due to surface potentials directly under the probe tip, as extracted from $\Phi_{KP}(x)$ using $\alpha_i(x)$ from Fig. 4.2. (c) After subtracting the $V_D = 0$ background variations, differential potentials highlight the true, dissipative potential drops along the SWNT. The inset shows low bias data at higher magnification.

to the gate electrode and $\alpha_G$ approached 1.0. Approaching the source or drain, $\alpha_G$ dropped to zero and these electrodes began to dominate the measured $\Phi_{KP}$. The most important feature of the $\alpha$ images is not these average values but rather the empirical functional form
of their spatial variation. For example, beginning from a value of 1 at the electrode edge, 
\( \alpha D(x) \) falls approximately as \( e^{-x/L} \) with a characteristic length \( L = 140 \) nm. This rapid variation normally precludes quantitative KPFM analysis, since it causes spatial variation of \( \Phi_{KP} \) even when the probe is over regions of uniform potential and work function.

Close to the SWNT, a third coefficient \( \alpha_{SWNT}(x) \) couples the probe to the main potential of interest \( V_{SWNT} \). \( V_{SWNT} \) is proportional to \( V_D \), so the single derivative \( \partial \Phi_{KP} / \partial V_D \) measured over the SWNT is a weighted combination of both \( \alpha_{SWNT} \) and of \( \alpha_D \). Nevertheless, data directly over the SWNT and parallel to the SWNT but displaced by 500 nm provides enough information to effectively separate the two contributions and produce the plot of \( \alpha_{SWNT} \) shown in Fig. 4.2(b). At its maximum, \( \alpha_{SWNT} \) averaged 0.7 This value is substantially larger than the 0.2 reported by Brunel et al. [15], perhaps because of the increase in \( \alpha_{surface} \) associated with the FM mode used here [189]. Directly over the SWNT and far from the electrodes, \( \alpha_G \) averaged only 0.3 and we estimate that direct coupling to the distant source and drain electrodes contributed less than 3 % to \( \Phi_{KP} \). Perpendicular to the SWNT, \( \alpha_{SWNT} \) falls exponentially with nearly the same characteristic length \( L \) as at the electrode edge, indicating that the rapid growth of \( \alpha_G \) dominates in both cases. Fig. 4.2(c) shows line cuts of each \( \alpha_i \) directly along the SWNT and their sum \( \alpha_{total} \), which deviates less than \( \pm 5\% \) from unity and confirms that all of the primary couplings have been accounted for.

Knowing each coupling factor \( \alpha_i(x, y) \) makes it straightforward to isolate the desired surface potential from raw \( \Phi_{KP}(x, y) \) data. Fig. 4.3 depicts this process by showing line cuts of \( \Phi_{KP}(x, V_D) \) extracted along the SWNT [Fig. 4.2(a)] and the potential \( V_{SWNT}(x, V_D) \) calculated using the spatially-varying \( \alpha_{SWNT}(x) \) [Fig. 4.2(b)]. In this data, \( V_{SWNT}(x, V_D) \) is the more accurate potential measurement (lateral resolution of \( \approx 50 \) nm is limited by a finite tip radius, but independent techniques can further improve upon this aspect [158, 110, 74]). We note some of the important differences between \( \Phi_{KP}(x, V_D) \) and \( V_{SWNT} \). Firstly, the flatness of \( \Phi_{KP}(x, V_D = 0) \) has been interpreted in previous work on SWNTs
as an indication that SWNT are quasi-ballistic, with minimal dissipative scattering. More correctly, $V_{SWNT}(x, V_D = 0)$ has a broad central maximum that is 0.4 to 0.6 V higher in potential than either end. This broad maximum is in better agreement with a bandstructure model, reflecting both a work function dissimilarity and the electrostatically-induced carriers and band bending that result from the applied $V_G$. Secondly, we note a steep drop in $\Phi_{KP}(x, V_D = 1.5 V)$ near the drain electrode that is typically ascribed to contact resistance at the SWNT-electrode interface. That drop vanishes in the corresponding $V_{SWNT}(x, V_D = 1.5 V)$, proving that it actually results from the steep variations of $\alpha_i(x, y)$ that occur over $0 < x < 250$ nm.

Potential corrugations are observed along the SWNT in both $\Phi_{SWNT}(x, V_D)$ and $V_{SWNT}(x, V_D)$, and these are primarily caused by a fourth coupling term $\alpha_{oxide} V_{oxide}$. This term includes the weak but spatially-varying contributions from charged surface contaminants and traps in the SiO$_2$. Previous research using scanning photocurrent microscopy has studied these traps, their optical excitations, and their effects on SWNT transport. In KPFM, inhomogeneous point charges perturb $\Phi_{KP}(x, y)$ with a spatial dependence that is distinct from either $\alpha_{SWNT}$ or $\alpha_G$ and with virtually no dependence on $V_D$. These attributes allow the $\alpha_{oxide} V_{oxide}$ contribution to be easily separated and directly imaged when a wider range of $V_G$ values are used. Here, no separation has been attempted, in part because the low-bias perturbations of point charges on SWNTs have been previously reported in detail [181, 41, 42]. As a result, the $\alpha_{oxide} V_{oxide}$ contributions cause variations of the weighted couplings $\alpha_G$ and $\alpha_{SWNT}$ [Fig. 4.2(c)] and potential perturbations along the SWNT [Fig. 4.3(b)], even though the capacitive couplings $\partial^2 C_G / \partial z^2$ and $\partial^2 C_{SWNT} / \partial z^2$ are constant along the SWNT channel. At room temperature, charges on the surface become mobile and can act to screen the probe potential $V_\omega$, but high frequency excitation in conjunction with high speed imaging may obviate this effect.

Rather than focusing on the perturbations caused by point charges, we instead focus on the
$V_D$-dependent potential gradient along the SWNT channel. We subtract the background potential $V_{SWNT}(x, V_D = 0)$ from every measurement of $V_{SWNT}(x, V_D \neq 0)$, thereby removing $\alpha_{oxide} V_{oxide}$ perturbations and highlighting the current-induced gradients caused by dissipative scattering, which are features of more general interest to the nanoscale device community.

Fig. 4.3(c) shows the resulting difference plots $\Delta V_{SWNT}(x, V_D)$, indicating the potential drops that occur when currents flow through the SWNT. Nine values of $V_D > 0$ are shown in Fig. 4.3(c), and additional measurements at $V_D < 0$ and with source and drain electrodes reversed were complementary. Overall, the $\Delta V_{SWNT}(x, V_D)$ curves are smooth and monotonic. Each curve has a wide, central region with a uniform slope, consistent with a constant scattering rate or resistance per unit length. This resistance per unit length is most clearly illustrated by plotting the mean slope $d\Delta V_{SWNT}/dx$ versus the current $I_D$ for each value of $V_D$, as shown in Fig. 4.3 (squares). The linear dependence indicates ohmic dissipation along the SWNT channel. The mean slope of 70 kΩ/μm corresponds to a mean free path of 90 nm, a channel resistance of 150 kΩ, and contact resistance of 220 kΩ. Identical experiments performed on a semiconducting SWNT observed a higher average resistivity of 170 kΩ/μm corresponding to a mean free path of 38 nm (Fig. 4.4, circles), a channel resistance of 545 kΩ and a contact resistance of 55 kΩ.

These values are in excellent agreement with the SWNT transport literature [12], particularly the finding of shorter scattering lengths in semiconducting SWNTs [117]. The notable aspect of this agreement is that FM-KPFM makes accurate and quantitative measurements accessible from a single device. Mean free path measurements typically require arrays of devices fabricated with different source-drain separations, so that scattering per unit length can be isolated from contact effects [147, 39]. Quantitative FM-KPFM obtains the same information from short segments of a single device. Besides efficiency, this fact allows FM-KPFM to directly image anomalous resistances or device-specific behaviors [40], including
Figure 4.4: Drain current versus average potential gradient for two types of SWNTs. A fit to each data set (solid lines) determines the average resistance per unit length, independent of any contact resistance.

those which cannot be accounted for by scanned probe techniques that do not spatially resolve potential profiles [80, 81, 183].

Closer to the drain and source electrodes, the $\Delta V_{SWNT}(x, V_D)$ curves in Fig. 4.3(c) become steeper. Contact resistance should, in fact, cause abrupt drops at the metal-SWNT interfaces, perhaps broadened by a combination of the KPFM lateral resolution and the extended depletion widths of SWNTs [106]. Unfortunately, these contact effects also occur in the regions where $\alpha_D$ and $\alpha_{SWNT}$ are most steeply varying and not fully separable. Additional investigation of these effects might benefit from measurements on devices having high contact resistances or gate-tunable Schottky barriers.

4.5 Conclusion

In conclusion, we have demonstrated a FM-KPFM technique that quantitatively measures surface potentials and resistivity along current-carrying nanodevices. The method does not
rely on high aspect ratio tips or complex numerical simulations to reconstruct the potentials of interest, but rather removes artifacts empirically by directly measuring the coupling factors $\alpha_i$ and their spatial variation. The technique was demonstrated on isolated SWNTs as an extreme case of particularly weak coupling to the probe, but is versatile enough for arbitrary device geometries and other electronic systems of similar complexity. The method can probably benefit any open- or closed-loop electrostatic imaging mode, including electrostatic force microscopy (EFM) and amplitude-modulated KPFM.
Chapter 5

Mean free paths in single-walled carbon nanotubes measured by Kelvin probe force microscopy

The inelastic mean free path $\lambda_{MFP}$ is a critical parameter for electronic devices. Here, we demonstrate Kelvin probe force microscopy (KPFM) as a technique for studying $\lambda_{MFP}$ in biased, semi-metallic single-walled carbon nanotubes (SWNTs). Having one of the longest room-temperature $\lambda_{MFP}$ values of any known material, SWNTs provide a unique platform for probing mesoscopic transport. KPFM directly determined $\lambda_{MFP}$ as a function of bias, quantitatively determined the contributions of different scattering mechanisms, and enabled comparative study of individual SWNTs with and without disorder. The room-temperature mean free paths for optical phonon and surface polar phonon scattering were measured to be $62 \pm 20$ nm and $260 \pm 50$ nm, respectively. The optical phonon scattering length is significantly longer than inferred from previous measurements, and it resolves a longstanding discrepancy between SWNT theory and experiment, suggesting that KPFM could become
a preferred quantitative technique for studying transport in nanoscale systems.\footnote{Reprinted with permission from "Mean free paths in single-walled carbon nanotubes measured by Kelvin probe force microscopy" by E.J. Fuller, D. Pan, B.L. Corso, O.T. Gul and P.G. Collins \textit{Physical Review B} 89(24):245450, 2014. Copyright, American Physical Society.}

## 5.1 Background

The inelastic mean free path $\lambda_{MFP}$ of a conductor is determined by the scattering mechanisms relevant to its electronic resistance. For most materials, acoustic phonon (AP) scattering is the dominant mechanism, limiting room-temperature $\lambda_{MFP}$ values to be much less than typical device lengths. Single-walled carbon nanotubes (SWNTs), on the other hand, are quasi-one-dimensional conductors with minimal AP scattering [3, 117]. The suppression of AP scattering allows SWNT devices to remain quasiballistic up to room temperature, which is consequential for practical applications and enabling for the investigation of fundamental scattering mechanisms in reduced dimensions.

Traditionally, $\lambda_{MFP}$ is deduced from length-dependent conductivity, as measured versus bias, temperature, and other parameters. The $\lambda_{MFP}$ in SWNTs has been studied this way using many pairs of device electrodes patterned along a mm-long SWNT [147, 39]. Additionally, SWNTs high-bias $\lambda_{MFP}$ has been inferred by comparing current-voltage curves to models [185, 76, 144]. However, both transport-based techniques require assumptions about SWNT contact resistance, temperature profiles, and substrate disorder. Furthermore, SWNTs are famously variable, with electronic properties that depend sensitively on chirality, disorder, and the surrounding environment. Fabricating arrays of devices, especially devices that are long enough to be diffusive, is an impractical method of understanding SWNT variability in submicrometer devices.

Recent advances in frequency-modulated Kelvin probe force microscopy (FM-KPFM) now provide the sensitivity to image electrostatic potentials with sub-nm resolution [152, 56],
and we have reported a frequency-modulated, parameterized FM-KPFM technique for reproducible, quantitative imaging of nanoscale current-carrying devices [50]. Past studies using KPFM and related techniques like electrostatic force microscopy (EFM) have imaged SWNTs in order to probe local density of states [62], band structure [11], and electrostatic gating [133], but quantitative imaging of dissipation in current-carrying SWNTs has proven challenging [15, 121, 95, 73, 74, 2]. The small diameter (1 nm) and low carrier density (1 - 100 µm\(^{-1}\)) of SWNTs make coupling to scanning probes especially weak and subject to artifacts arising from long-range electrostatic coupling to device electrodes [15, 121, 95] and to charges on a supporting substrate [73, 74]. Here, we apply the parameterized FM-KPFM technique to directly extract \(\lambda_{MFP}\) from small sections of a single SWNT, independent of contact resistance or other device modeling.

5.2 Results

FM-KPFM images were acquired in a high-vacuum, variable-temperature instrument (JEOL JSPM-5200) at \(10^{-7}\) Torr. Thin-film resistors patterned alongside the SWNT devices determined the operating surface temperature to be 185 K. Semi-metallic SWNTs with minimal gate dependence were selected for this study and then imaged at a bias \(V_G = -1\) V that provided good contrast between the SWNT and SiO\(_2\) substrate. Figure 5.1(a) depicts the measurement geometry and applied biases. During imaging, individually sweeping \(V_S\), \(V_D\), and \(V_G\) produced a parameterized FM-KPFM set of images that were used to extract the coupling of the SWNT to the tip at every pixel [50]. The enhanced resolution of FM-KPFM and the parameterization technique combined to produce quantitative measurements of SWNT potential that were significantly improved over previous, uncalibrated EFM work [11, 15, 121, 73, 74, 9, 135, 131].

Figure 5.1(b) depicts raw KPFM images of a typical SWNT device with a diameter of 1.9 nm.
Figure 5.1: (a) Schematic of the measurement apparatus. (b) Set of FM-KPFM images characterizing voltage drops along a SWNT channel, with topography on the left and $V_{KP}$ plotted on a color scale for three different $V_D$ values.

The grayscale image (left) corresponds to topography, while three color scale images (right) depict $V_{KP}(x,y)$ at different source-drain biases. Figure 5.2(a) depicts corrected surface potential profiles $\Delta V_{SWNT}(x)$, where $x$ now refers to distance along the SWNT from drain ($x = 0$) to source. $\Delta V_{SWNT}(x)$ was calculated as the difference $V_{KP}(x,V_D) - V_{KP}(x,V_D = 0)$ in order to highlight the current-induced potential gradient and eliminate underlying variations caused by charge traps in the SiO$_2$. An additional factor $\alpha(x)$ was also used to correct for spatial variations in the capacitive coupling between probe and SWNT, as described in detail previously [50, 95, 94].

The $\Delta V_{SWNT}(x)$ curves in Fig. 5.2(a) resolve a combination of steep drops near the electrodes, homogeneous gradients $dV/dx$ along the SWNT, and short-wavelength troughs and peaks. The analysis below is entirely focused on the average gradient $dV/dx$, but first we briefly describe the other two components. The sharp potential drops at $x = 0$, and $x = 1.75 \mu$m reflect contact resistance effects. The raw data cannot be easily converted into
reliable contact resistance values because the magnitude and shape of $\Delta V_{SWNT}(x)$ near the electrodes convolve true surface potentials with sharply changing capacitive couplings that occur in these regions [50]. At the contacts, the electrode and SWNT potentials are difficult to separate, so KPFM provides limited new insights. Similarly, fluctuations of $\pm 50$ mV are caused by randomly distributed SiO$_2$ charge traps that have spatially varying couplings. Subtraction of the $V_{KP}(x, V_D = 0)$ baseline is a good first-order correction for isolating the effects of these traps, but it is incomplete because the accumulation and depletion of traps is bias-dependent. This bias dependence results in induced potentials and memory effects, the study of which dominate previous KPFM work reported on SWNTs [73, 74]. Without considerable, device-specific modeling of a surface, it is difficult to distinguish these artifacts from more fundamental, current-induced oscillations such as Landauer oscillations [187].

In contrast to the two types of features described above, the average gradient $dV/dx$ provides definitive, quantitative information about dissipation along a SWNT that is relatively independent of the supporting surface. Figure 5.2(b) plots $dV/dx$ versus $I_{SD}$ for the six curves in Fig. 5.2(a) and three additional, higher bias curves not shown. For each data point, $dV/dx$ was determined from a linear fit of $\Delta V_{SWNT}(x)$ from $x = 0.3$ to $x = 1.3$ $\mu$m, the region of constant $\alpha(x)$ (as determined by the parameterized-KPFM technique [50]). The data in Fig. 5.2(b) determine the differential resistance per unit length, $R/L = I_{SD}^{-1}dV/dx$. At low bias, $R/L = 7$ k$\Omega$/\$\mu$m, corresponding to a channel resistance of 12 k$\Omega$ with contact resistance of 31 k$\Omega$. At high bias, the channel resistance increased to 75 k$\Omega$ at fields of 1.0 V/$\mu$m.

The direct measurement of $dV/dx$ by KPFM is a significant improvement over traditional transport experiments. Because of contact resistance, only a portion of the applied bias drops along the SWNT channel, and the appropriate fraction must be estimated in two-terminal characterization. As an example of the difference, Fig. 5.2(b) compares the KPFM data against estimates of $dV/dx$ calculated from the $I_{SD}(V_D)$ characteristics of the same SWNT. The simplest case assumes no contact resistance (blue squares); therefore, it overestimates
Figure 5.2: (a) Line cuts taken from FM-KPFM images along a SWNT from drain ($x < 0$) to source ($x > 1.7 \, \mu m$). Each curve corresponds to a single KPFM image acquired at a particular $V_D$.  

(b) Average channel field $dV/dx$ determined within the uniform portion of the channel $0.3 > x > 1.3 \, \mu m$, plotted versus $I_{SD}$ (red circles). For comparison, a two-terminal field estimate $V_D/L$ (blue squares) overestimates the field at each bias due to contact resistances. Shading highlights the error from the contact effect and the bias dependence of its fractional effect.

the true $dV/dx$ at all biases. Accurate estimation of the contact resistance can reduce the error only if the model correctly predicts its dependence on bias. Contact resistances determined from KPFM profiles were found to vary nonmonotonically with bias by 20%. This field-dependence of contact resistance is very difficult to measure by any other method,
even in arrays of devices having different channel lengths, and no models currently predict contact resistances for metallic SWNTs [89, 28]. KPFM is unique in revealing both the channel dissipation \(dV/dx\) and these contact-resistance components.

## 5.3 Analysis and Modeling

Having successfully removed contact effects, \(dV/dx\) can be directly interpreted as a measure of \(\lambda_{MFP}\). In the Landauer-Büttiker formalism, \(\lambda_{MFP} = R_Q I_{SD}/(dV/dx)\), where \(R_Q = (4e^2/h)^{-1}\) is the reciprocal of the SWNT quantum conductance [29]. Figure 5.3 depicts \(\lambda_{MFP}\) versus \(dV/dx\) for the data in Fig. 5.2 (SWNT A) and for four other SWNT channels of varying chirality, diameter, and disorder (SWNTs B, C, D, and E). SWNTs A and B are remarkably similar, despite having very different diameters of 1.9 and 1.2 nm; both show a strong bias dependence, with \(\lambda_{MFP}\) dropping nearly tenfold from 0.1 to 1.0 V/\(\mu\)m. These examples will be analyzed in detail before discussing the disorder-limited \(\lambda_{MFP}\) values of SWNTs C, D, and E.

In addition to \(\lambda_{MFP}\), the gradient \(dV/dx\) also determines the local joule heating per unit length \(I_{SD}(dV/dx)\) and provides the means to estimate the SWNT temperature \(T\). In steady-state equilibrium and far from contact effects, \(T\) is determined by the thermal coupling \(g\) to the supporting SiO\(_2\) substrate and the substrate temperature \(T_0 = 185\) K, according to the expression \(T = T_0 + I_{SD}(dV/dx)/g\). The parameter \(g\) has been investigated experimentally and theoretically for SWNTs, and it is believed to have values of \(0.2 - 0.3\) W/mK on smooth SiO\(_2\) substrates [144, 146, 116]. Experimental \(g\) values vary widely in the literature because effects like surface chemistry [132] and surface roughness can both affect the exact value. In general, \(g\) is highest for very smooth substrates, on which SWNTs have the greatest contact areas.
Figure 5.3: Experimental $\lambda_{MFP}$ determined from KPFM potential profiles, plotted versus field for two high quality SWNTs (A, B) and three SWNTs limited by disorder (C, D, and E). Solid line depicts the theoretical fit to scattering mechanisms described in the text.

The SWNT temperature $T$ is a key element for interpreting $\lambda_{MFP}$ in terms of fundamental scattering mechanisms because each mechanism has characteristic thermal statistics. The bias dependence of $\lambda_{MFP}$ in Fig. 5.3 reflects self-heating of the SWNT and these underlying statistics. For example, we consider three mechanisms that have been extensively modeled in the SWNT literature. AP scattering has a weak contribution to $\lambda_{MFP}$ because of the restricted phase space for backscattering in SWNTs [117]. At low bias, the primary mechanism limiting $\lambda_{MFP}$ is surface polar phonon (SPP) scattering induced by the supporting SiO$_2$ substrates [142]. The low bias $\lambda_{MFP} \approx 1 \mu$m in Fig. 5.3 is consistent with previous studies of this SPP mechanism [18]. At higher bias, $\lambda_{MFP}$ decreases due to additional scattering by low-momentum optical phonons (OPs) [185, 76, 144, 135]. Matthiessen’s approximation may be used to express $\lambda_{MFP}$ in terms of a characteristic scattering length for each mechanism, 

$$\lambda_{MFP} = (\lambda_{AP}^{-1} + \lambda_{SPP}^{-1} + \lambda_{OP}^{-1})^{-1}.$$ 

We reproduced standard SWNT modeling methods to extract individual scattering lengths $\lambda_{AP}$, $\lambda_{SPP}$, and $\lambda_{OP}$ from the KPFM data using the expressions above for $T$ and $\lambda_{MFP}$. 

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Each scattering length was expressed as \( \lambda_i = \lambda_{i,300}n_i(300)/n_i(T) \), where \( \lambda_{i,300} \) was the room temperature value and \( n_i(300)/n_i(T) \) was the temperature-dependent number ratio of the relevant phonon population with appropriate statistics. This approach has proven useful in previous studies by allowing for immediate comparisons among theoretical and experimental values of \( \lambda_{i,300} \) [143]. The population \( n_{AP}(T) \) was semiclassical and linear in temperature, whereas \( n_{OP}(T) \) and \( n_{SPP}(T) \) followed Bose-Einstein statistics. The OP modes were assigned an average energy \( \hbar\omega_{OP} = 0.18 \) eV, and modeling included absorption, emission, and a dependence on \( dV/dx \) as described in a previous study [144]. For SPP scattering, we included all five surface modes \( \hbar\omega_{15} \) and used the phonon energies and Fröhlich couplings calculated by Perebeinos et al [137].

Since all of the characteristic energy scales \( \hbar\omega \) are well established for SWNTs, the four free parameters in the model were the room temperature values \( \lambda_{AP,300} \), \( \lambda_{SPP,300} \), and \( \lambda_{OP,300} \), and the thermal coefficient \( g \). Of these, \( \lambda_{SPP,300}, \lambda_{OP,300}, \) and \( g \) have shown the greatest uncertainty and variability in the literature. Fitting these three variables to KPFM data proved to be insensitive to the exact value of \( \lambda_{AP,300} \), reflecting the relatively insignificant contributions of \( \lambda_{AP} \) over the experimental range of \( dV/dx \) and \( T \). Consequently, we assigned \( \lambda_{AP,300} \) to be 1.8 \( \mu \)m [144, 135, 187] and performed a least-squares fit to the other three parameters. Figure 5.3 shows the results (red line) of fitting the model to KPFM data for SWNT A and highlights the agreement at high bias (inset). The process yielded \( g = 0.28 \pm 0.05 \) W/mK, \( \lambda_{SPP,300} = 0.26 \pm 0.05 \) \( \mu \)m, and \( \lambda_{OP,300} = 62 \pm 20 \) nm, with a reduced chi-squared error \( \chi_R = 0.8 \). Each uncertainty is stated as one standard deviation calculated from the uncertainty in \( \lambda_{MFP} \) with all other parameters held constant; therefore, each is an overestimate of the lesser, covariant error. Within the limits of the data set, \( \lambda_{MFP} \) is identical for SWNTs A and B, indicating that the component scattering lengths are not strongly diameter-dependent for semi-metallic SWNT.

Figure 5.4 uses the results of the fitting to depict the composition of \( \lambda_{MFP} \). At fields
< 0.14 V/µm, λ_{SPP} is the shortest scattering length, and it limits λ_{MFP}. Above 0.14 V/µm, the significance of λ_{SPP} diminishes as the steeply falling λ_{OP} becomes limiting. At fields > 0.3 V/µm, spontaneous OP emission accounts for most of λ_{MFP} and the shape of its bias dependence. The thermal coupling g = 0.28 W/mK agrees with previous experimental measurements and theoretical models, allowing us to confidently predict the rise in temperature that accompanies higher fields. A temperature variation of ≈ 80 K is the primary cause of changes in λ_{SPP}, and including self-heating is important for obtaining a good fit between the model and KPFM data; on the other hand, the temperature plays a minimal role in OP emission or the overall shape of λ_{MFP}. The case can be very different for weakly coupled substrates or suspended SWNTs, where highly nonequilibrium phonon temperatures cause negative differential conductance features not observed here [143].

![Graphical decomposition of λ_{MFP} into each contributing scattering mechanism. The corresponding rise in temperature T, as calculated from self-heating considerations, is approximately 80 K at a field of 1 V/µm (dashed line).](image)

The scattering length λ_{SPP,300} = 0.26 µm agrees with previous two-terminal studies of low bias scattering [147]. Rotkin et al. have proposed that SPP scattering might not contribute to SWNT heating, since the energy dissipation in this mechanism is directed into substrate...
phonons [149]. To consider this possibility, we modified our model to exclude any self-heating from SPP dissipation. Fitting the same KPFM data to this new model left $\lambda_{SPP,300}$ unchanged and resulted in a fit that was indistinguishable from the curve in Fig. 5.3. However, the new fitting produced values of $g = 0.49 \pm 0.05$ W/mK and $\lambda_{SPP,300} = 38 \pm 15$ nm. The principle of excluding SPP self-heating seems logical, but the resulting fit for $g$ is almost twice as high as has been found in previous experimental and theoretical work. Understanding this discrepancy requires further investigation, and it may indicate that SPP modes remain in thermal equilibrium with a SWNT.

Experiment and theory disagree significantly over the correct value of $\lambda_{OP,300}$ in SWNTs. First-principles models predict $\lambda_{OP,300}$ over a range from 40 – 180 nm [3, 180, 136, 102], whereas most experimental studies have reported values of only 10 – 15 nm [185, 76, 135, 77, 78, 193]. Our value $\lambda_{OP,300} = 62$ nm is 50 nm larger than previous experimental work, though still less than early theoretical predictions. Most past experiments have been based on two-terminal $I_{SD}(V_D)$ characteristics, which provide very indirect measurements of $\lambda_{OP,300}$ and have limited accuracy in terms of modeling SWNT contact resistance and contact self-heating [144]. Furthermore, early experimental work predated the appreciation of SPP mechanisms in SWNTs. More recent optical studies on bulk SWNT bundles have extrapolated values of $\lambda_{OP,300}$ as large as 40 nm but concluded the results were only qualitative for single SWNTs [97]. By comparison, KPFM directly measures $\lambda_{MFP}$ in a single SWNT, and in the high bias regime $\lambda_{MFP}$ is largely determined by the single free parameter $\lambda_{OP,300}$.

Recent theoretical work by Lazzeri et al. [102] invoked nonequilibrium phonon populations $n_{OP}$ to explain the disagreements between theory and experiment. OP temperatures exceeding 6000 K enhanced OP scattering and were one method of accounting for experimental $\lambda_{OP,300}$ values as short as 15 nm. While 6000 K may be unrealistically high, the same calculations predicted that phonon temperatures $< 1900$ K would reduce $\lambda_{OP,300}$ from 120 – 60 nm, the value measured here by KPFM [102]. Raman spectroscopy of individual SWNTs
at high bias has demonstrated nonequilibrium OP temperatures of 1500 K [169], suggesting that the KPFM experiments are in complete agreement with theory.

Next, we discuss SWNTs C, D, and E in Fig. 5.3. In comparison to SWNTs A and B, these three samples each had small $\lambda_{MFP} < 250$ nm with minimal bias dependence. SWNTs C and D had diameters of 1.1 and 1.5 nm, comparable to SWNTs A and B, whereas SWNT E had an unusually large diameter of 2.6 nm. The KPFM profiles $\Delta V_{SWNT}(x)$ of SWNTs C, D, and E were all similar to those for SWNT A in Fig. 5.2, showing uniform, monotonic dissipation along each channel but with steeper slopes $dV/dx$ for a given $I_{SD}$ that resulted in smaller $\lambda_{MFP}$ values. We note the advantage of KPFM in distinguishing these high-resistance SWNT channels from mere bad contacts that might also give sample-to-sample variability.

Modeling the $\lambda_{MFP}$ for SWNTs C, D, and E can be accomplished by adding a sample-dependent, bias-independent scattering length $\lambda_{disorder}$ to the model. This empirical $\lambda_{disorder}$ term accounts for extrinsic disorder that might be caused by contamination from CVD catalysts or photolithography residues along the SWNT-substrate interface [178]. Either long-range or poorly screened, short-range disorder potentials could provide new energy dissipation channels, and these shunt the intrinsic OP scattering mechanism when $\lambda_{disorder}$ is sufficiently short. Disorder, and especially disorder from charged contaminants, is spatially inhomogeneous on the shortest length scales, but KPFM as practiced here has a $\approx 40$ nm resolution that spatially averages the effects of point sources. We define $\lambda_{disorder}$ as the extrinsic source of uniform gradients in $\Delta V_{SWNT}(x)$ and assume that a small $\lambda_{disorder}$ is indicative of a dense background of such contaminants. This definition is distinct from isolated point defects, which introduce highly nonuniform effects like localized potential steps [48] that are beyond the scope of this report. None of the SWNTs A-E exhibited steps or staircases in $\Delta V_{SWNT}(x)$ that might indicate isolated, strongly scattering sites.

At high bias, the $\lambda_{MFP}$ of SWNTs A-E are almost indistinguishable. Consequently, high bias
resistance does not distinguish disordered SWNTs from pristine SWNTs, even though the underlying mechanisms are very different. This finding suggests that large-scale integration of SWNTs as transistors or interconnects at digital voltages (i.e., > 1 V/µm) [160] might prove insensitive to many types of disorder. This conclusion is very promising for applications, but it also illustrates how electronic uniformity in wafer-scale testing does not imply high quality SWNT material or even uniform underlying properties. Distinguishing disordered SWNTs from pristine ones requires measurements of the low bias temperature dependence or else transport noise, techniques that are very rarely applied to large arrays of devices.

Although semi-metallic SWNTs were the focus of this paper, preliminary KPFM measurements on semiconducting SWNTs suggest an even greater sensitivity to disorder than in metallic SWNTs, as previously predicted [3, 117]. SWNTs C, D, and E illustrate the difficulty of probing the physics of scattering in the disordered limit, since $\lambda_{MFP}$ no longer exhibits bias- or temperature-dependence. Nevertheless, previous transport studies have reported significant differences between metals and semiconductors at low fields [147, 39], and theoretical calculations predict that $\lambda_{MFP}$ should be sensitive to carrier concentration and chirality in semiconducting SWNTs [138]. KPFM provides new opportunities to study these effects.

In conclusion, KPFM directly resolved high- and low-bias dissipation in individual SWNTs. KPFM data determined $\lambda_{MFP}$ as a function of $dV/dx$ for individual SWNTs without assumptions about contact resistance or contact heating, which greatly simplified a comparison among different devices and the fitting of experimental data to first-principles models for each scattering mechanism. We observed $\lambda_{SPP,300} = 0.26 \pm 0.05 \mu m$ and $\lambda_{OP,300} = 62 \pm 20 nm$, the latter of which is 50 nm longer than previously estimated by two-terminal transport experiments but in much better agreement with theoretical models. A comparison of SWNTs with and without homogeneous disorder indicated that such disorder was inconsequential above 1 V/µm, a promising finding for digital electronics based upon SWNT devices.
Chapter 6

Distinguishing carbon nanotube defect chemistry using scanning gate spectroscopy

Electronic scattering at individual defect sites is presumably sensitive to defect chemistry. Here, we combine advances in carbon nanotube device fabrication and scanning probe characterization to investigate this correspondence. Specifically, we apply scanning gate spectroscopy (SGS) to the study of defects introduced into single walled carbon nanotubes by point functionalization in water, sulfuric acid, or hydrochloric acid. SGS measures the energy-dependent transmission functions of defect sites, and by working in the dilute limit of individual, isolated defects we empirically distinguish the three chemical types. A preliminary analysis proposes a scattering model in order to motivate further theoretical investigations of this one-dimensional scattering system. \(^1\)

6.1 Background

Historically, optical spectroscopy has been the primary tool for characterizing point defects [55, 33]. With the continued scaling of electronic devices, however, defect properties are now becoming directly accessible to electrical transport measurements. Various types of devices, including traditional Si field effect transistors (FETs), are now fabricated at scales for which the presence of a single atomic defect affects the device conductance, mobility, or fluctuations and noise [91]. Using high-purity devices made of Si, Ge, diamond, or compound semiconductors, a nascent field is growing around the concept of single atom electronics, sometimes termed solotronics [93, 45].

Of the different low-dimensional conductors that are most sensitive to defects, the single walled carbon nanotube (SWNT) is an exceptional case. Pristine SWNTs are quasi-one-dimensional conductors with inelastic mean free paths that approach 1 µm at room temperature [147, 109], and these characteristics make their electronic properties unusually sensitive to individual defects [23]. The quasi-one-dimensionality of SWNT states means that every carrier propagating through the device is able to interact with the defect potential. The long mean-free path allows SWNT devices to be easily fabricated using conventional lithography, but still in a regime where other sources of inelastic scattering and dissipation are minimal. Besides these two advantages, the versatility afforded by carbon chemistry makes SWNTs a rich system where defect scattering sites can be chemically tailored to have many possible identities. Whereas traditional semiconductor defects are most likely to be atomic vacancies or interstitials, a SWNT defect site can incorporate an almost unlimited variety of covalently-bonded molecules [10, 163], and consequently, a range of scattering potentials. This versatility provides an opportunity for precisely mapping the correspondence between chemical structure and electronic function in the challenging limit of dilute disorder. Near-field optical techniques can locate individual defects, but not distinguish the properties of different chemical types [59, 26]. Transport measurements, on the other hand, are sensitive
to individual defects, especially in the quasi-ballistic limit where one defect is the primary source of resistance [109, 54, 111]. This sensitivity provides a possible experimental method for identifying and categorizing different types of defects.

In order to test this hypothesis and characterize SWNT defects electronically, we developed the electrochemical technique of point functionalization [54] to add individual point defects to operational SWNT FETs. By measuring the same SWNT before and after deliberate chemical modification, we can directly observe the change in electrical characteristics caused by the added disorder. To spatially resolve these effects and more precisely investigate the role of the defect sites, we combine the electrical measurements with simultaneous scanning probe interrogation [84]. An electrostatic potential $V_{\text{tip}}$ on a conductive, scanning probe tip allows a SWNT to be locally gated, independently from the rest of the device. When performed using fixed biases, this scanning probe technique is known as scanning gate microscopy (SGM), and it creates a spatial image of the channel transconductance at particular bias conditions [14, 41, 83, 90, 103, 4, 66, 134]. We have combined SGM with more traditional SWNT transport spectroscopy [12, 109] by sweeping through multiple values of the backgate bias $V_{\text{bg}}$, source-drain bias $V_{\text{sd}}$, or $V_{\text{tip}}$ at each position along a SWNT. This technique generates a multidimensional data set referred to as scanning gate spectroscopy (SGS). The SGS data provides a detailed record of the gate-dependent scattering that occurs in the immediate vicinity of a defect site [69].

In this paper, we summarize the results of performing scanning gate spectroscopy on a variety of SWNT devices. A single defect has been analyzed in detail in a previous publication [69], but here we describe the technique and apply it comparatively to SWNTs oxidized to different degrees in water or acids. This report focuses on defects produced using oxidation in DI water (18 Ω, Nanopure), concentrated sulfuric acid (18 M H$_2$SO$_4$), or concentrated hydrochloric acid (12 M HCl). Evidence exists for associating H$_2$O oxidation with -OH adducts, H$_2$SO$_4$ oxidation with ethers and epoxides, and HCl oxidation with -Cl adducts.
Nevertheless, the exact chemical nature is not the focus of this report, so the results and
discussion simply name the defects according to the starting electrolyte. Having oxidized
multiple devices in each electrolyte, we demonstrate typical scattering characteristics for
particular types of chemical modification. However, we also identify experimental variability
that must be controlled before chemically distinct defects can be reliably categorized.

6.2 Electrical Characterization and Scanning Gate Spectroscopy

Three-terminal FET characteristics were measured using dc and ac techniques over a tem-
perature range of 77 – 300 K. Point functionalized devices always exhibited a lowered con-
ductance $G(V_{bg}, V_{sd})$ at some backgate voltages $V_{bg}$, and this decrease grew stronger at lower
temperatures. Comparing $G(V_{bg}, V_{sd})$ characteristics before and after chemical modification
indirectly measured the electronic consequences of the added defects.

To spatially resolve these effects and more precisely investigate defect scattering, we acquired
SGM images of $G[V_{bg}, V_{sd}, V_{tip}(x, y)]$ by probing the SWNT with a conductive, scanning
probe. In this technique, the additional dc potential $V_{tip}$ on a probe tip allows small portions
of a SWNT to be electrostatically gated independently from the rest of the device. The
resulting SGM image is a real space representation of the modulation $\Delta G$ that occurs for
selected biases [84], and it has been established as a useful technique for identifying defects
[54, 41, 83, 90, 103, 36].

Figure 6.1(a) shows an example SGM image for a semiconducting SWNT (s-SWNT) device,
with the measurement geometry indicated in the inset. Dashed lines indicate the extent of
the source and drain electrodes, over which $V_{tip}$ has no effect on $G$ and the image is uniform.
Along the s-SWNT channel, the most prominent features correspond to Schottky barriers
where the SWNT meets the source and drain electrodes. A weaker, circularly symmetric feature near the middle of the image is the result of point functionalization. The image illustrates how SGM can confirm the presence of this added disorder, but the technique is clearly not sufficient to characterize the site quantitatively.

The scanning gate spectroscopy (SGS) technique [69] improves upon SGM by sweeping through multiple values of $V_{bg}$, $V_{sd}$, or $V_{tip}$ at selected tip positions, in order to study the scattering at such a site. Custom LabVIEW software allowed the AFM tip to be paused over predefined positions on the topographic image, in order to sweep $V_{bg}$ or $V_{tip}$ along the SWNT rather than at every pixel on the surface. Unless noted otherwise, all SGM and SGS images are acquired at a temperature of 130 K and pressure $<5 \times 10^{-7}$ Torr. Compared to ambient, these conditions greatly reduce noise and minimize hysteresis from mobile surface contaminants [103, 168].

As a multidimensional surface map, a SGS data set is more difficult to represent than a SGM image. In this report, all SGS data is represented by two-dimensional color plots of $G(\Delta x, V_{tip})$. The spatial coordinate $\Delta x$ in all of the images presented here corresponds to a line of pixels selected along the SWNT from source to drain electrode, while the second axis depicts the $V_{tip}$ dependence. Figure 6.1(b) provides an example SGS image for the same device as Fig. 6.1(a), illustrating the alignment of features along the spatial axis and the disappearance of features at progressively negative $V_{tip}$ values. The SGS information content along the $V_{tip}$ axis is the main focus of the results and discussion.

### 6.3 Results and Discussion

This report is primarily concerned with the SGS characterization of defects. The interpretation of SGS images is the focus of Secs. 6.3.1 and 6.3.2, with particular attention paid to the
Figure 6.1: (a) SGM and (b) corresponding SGS image of an s-SWNT having Schottky barriers at both electrodes and an additional, weakly scattering defect in the channel at $\Delta x = 1.2 \, \mu m$. Approximate position of source and drain electrodes are indicated with grey striping. Inset depicts the measurement geometry. (c) SGS for a similar s-SWNT over a different range of $V_{\text{tip}}$. (d) SGS image for a strongly scattering defect in a SWNT with only one sensitive interface. (e) SGS image for a pristine, small-bandgap SWNT that exhibits no appreciable Schottky barriers.

SWNT-to-SWNT variations that complicate direct comparisons among devices. Secs. 6.3.3 and 6.3.4 summarize the SGS differences that we attribute to defect chemistry, as achieved
by point functionalizing multiple devices in each of the three electrolytes studied. Finally, Sec. 6.3.5 addresses the consequences of unintended variations in the point functionalization technique.

6.3.1 Imaging of single defect sites

Even among straight, clean SWNTs of a particular class (metallic or semiconducting), significant differences arise in SGS data sets. Figure 6.1 depicts SGS images acquired on four s-SWNT devices, demonstrating some of this sample variability among s-SWNTs. In Fig. 6.1(b), a weakly scattering defect centered at $\Delta x = 1.2 \mu m$ is visible midway between two Schottky barriers. A second, nearly identical s-SWNT device has a weak feature at $\Delta x = 0.9 \mu m$ [see Fig. 6.1(c)]. A third s-SWNT exhibits much stronger contrast at its defect site [see Fig. 6.1(d)]. A comparison of the G and total modulation $\Delta G$ in each device shows that these parameters cannot be primarily responsible for the difference in defect contrast.

The main difference between these three examples is not the defect site per se, but the relative sensitivity of the Schottky barrier in each. In s-SWNTs, the electronic band gap is inversely proportional to diameter, and a lack of strong pinning by midgap states allows the Schottky barrier to vary freely from one device to another [61, 5]. Even when fabricated with the same contact metal, devices having slightly different SWNT diameters exhibit a range of Schottky barrier heights [172, 89, 21]. SWNT diameters of 1.0 – 1.3 nm have large Schottky barriers that dominate $G(V_{bg})$ characteristics and minimize the relative contribution from defects [see Figs. 6.1(b) and 6.1(c)]. SWNTs with larger diameters of 1.4 – 1.7 nm have smaller barriers that allow defects to contribute more to the total resistance or, in this case, to the enhanced contrast observed in Fig. 6.1(d).

Still larger SWNTs have vanishingly small Schottky barriers that are not effectively gated by the SGM or SGS techniques. Figure 6.1(e) depicts a defect-free s-SWNT with a diameter
of 2.0 nm, where Schottky barriers are not evident. Instead, the device has spatially uniform SGS modulation that is the hallmark of an intrinsic response of the SWNT band structure. Values of $V_{\text{tip}} > 1$ V locally deplete carriers and pinch off the channel equally well at any position along the SWNT. At $V_{\text{tip}} < 1$ V, the local accumulation of carriers does not enhance $G$, so that $G$ becomes nearly insensitive to the probe tip position. At intermediate values $-1 < V_{\text{tip}} < 1$ V, the response shown in Fig. 6.1(e) is fairly uniform, with slight variations arising from contaminants and inhomogeneities in the underlying SiO$_2$ [175, 181, 71].

In our experience, defects added to large diameter s-SWNTs like the one in Fig. 6.1(e) have been difficult to study. The scattering added by a defect is only observed at $V_{\text{tip}}$ values close to the band edge (i.e., $|V_{\text{tip}}| < 1$ V), where it is difficult to distinguish from substrate disorder. Furthermore, $G(V_{\text{tip}})$ data acquired directly over a defect site contains a mixture of contributions from both the defect and band structure depletion nearby. The minimal separation in $V_{\text{tip}}$ between the band edge and a defect limits our ability to isolate the defects energy-dependent contributions from other electrostatic effects [193]. By comparison, the spatially distinct features shown in Figs. 6.1(b)-6.1(d) provide much easier systems to analyze. Not only are the defects spatially separated from the Schottky barriers, but the band edges are fully outside the $V_{\text{tip}}$ measurement range. In small-diameter SWNT devices like these, defect contrast occurs at $V_{\text{tip}}$ values very close to the threshold for Schottky barriers and far from the band edges.

This empirical observation is an important point that merits emphasis. Each Schottky barrier or defect has a threshold $V_{\text{tip}}$ value above which it begins to reduce $G$. In Fig. 6.1(b), for example, the left and right Schottky barriers have thresholds of 0 and $-1$ V, respectively. The threshold of the defect response is slightly higher, in the range of $1.5 - 2$ V. In all three devices Figs. 6.1(b)-6.1(d) the defect threshold for sensitivity is found approximately $1.5$ V higher than the Schottky barrier threshold. This similarity is reproduced in a wide range of small diameter, oxidized s-SWNTs. The observation suggests that the chemical potential
of defect sites is pinned to a value set by the Schottky barrier threshold, at least in these cases where a strong Schottky barrier exists. This is very different from the case for larger diameter SWNTs, for which the Schottky barrier vanishes and defects are observed near the band edge. The interpretation of this difference is postponed to the next section, which first establishes $V_{tip}$ as a proper energy scale.

Finally, we note that it is very typical for the source and drain Schottky barriers in a device to be unequal, as observed in Figs. 6.1(b)-6.1(d). $V_{sd}$ does indeed break the symmetry of a device, but experiments reversing the bias prove that $V_{sd}$ is only one component of the observed difference. Experience suggests that the greater causes are extrinsic. The SWNT-metal interface is poorly defined by liftoff processing, prone to contamination, and very difficult to precisely characterize. Thus we have been led to ignore differences in these barriers and have instead focused on point functionalization performed in the central region of the FET channel.

### 6.3.2 Electrostatic analysis of single defect sites

When a defect is located far from an electrode or other gate-dependent site, it appears in SGM as a symmetric, circular feature and in SGS as a quasi-parabolic curve. These two are equivalent, and the former shape has been clearly described in the literature [41, 83, 90, 103]. The shape of features in an SGS image deserves special note, because the apparent defect size and explicit bias dependence in SGS images establishes the electrostatic coupling of the defect.

To model the effect of a defect on SGS imaging, we must consider both the geometry of this electrostatic coupling [see Fig. 6.2(a)] and the electronic structure of the defect itself. Due to evidence of Frenkel-Poole transport [115, 140], the defect is modeled as a localized state within a tunnel barrier that interrupts the SWNT band structure [see Fig. 6.2(b)].
The defect state itself extends around the SWNT circumference and some distance along the sidewall, but first-principles calculations predict various types of defects to have spatial extents of a few nm at most \([112, 192, 164, 104, 190]\), a scale ten times smaller than the lateral resolution of SGS. The defect state has a potential \(V_{\text{defect}}\) relative to the SWNT conduction band that is presumably sensitive to defect chemistry. In practice, however, this dependence is a constant offset that is secondary to the capacitive coupling of the defect to the back gate.
and probe tip. Movement of the probe tip and, more precisely, the charge $Q_{\text{tip}}$ located at the tip apex cause $V_{\text{defect}}$ to vary during SGS imaging. At fixed $V_{bg}$, the dependence is

$$V_{\text{defect}} = \frac{Q_{\text{tip}}}{4\pi\epsilon_o r} \quad (6.1)$$

where $r$ is the distance from tip apex to the relevant SWNT segment, and $\epsilon_0$ is the dielectric constant in vacuum. By evaluating $Q_{\text{tip}}$ in terms of the capacitance $C_{\text{tip} - \text{bg}}$ between the tip and back gate [155], and expressing $r$ in terms of its vertical and horizontal components, we arrive at the practical expression

$$V_{\text{defect}} = \frac{C_{\text{tip} - \text{bg}}(V_{\text{tip}} - V_{bg})}{4\pi\epsilon_o \sqrt{x^2 + y^2}} \quad (6.2)$$

Equation (6.2) predicts the specific dependence of $V_{\text{defect}}$ solely in terms of experimentally-controlled variables $x, z, V_{\text{tip}},$ and $V_{bg}$, where $x$ is the lateral distance to a defect site and $z$ is the height of the probe tip above the oxide surface. The sole unknown term in Eq. (6.2) is the capacitance $C_{\text{tip} - \text{bg}}$. This term has been extensively considered in the geometry of scanning probe tips because, for example, its value is necessary for the quantitative evaluation of SGM and other scanning probe images. Fortunately, $C_{\text{tip} - \text{bg}}$ depends logarithmically on $z$, so it is very nearly constant in this experimental geometry [155].

The raw SGM and SGS data measure conductance $G$ as a function of the same variables found in Eq. (6.2). However, analytical conversion of the $G$ data into $V_{\text{defect}}$ values is intractable without a priori knowledge of the analytical form of $G$. Instead of assuming a particular expression, we use a purely geometric argument to interconvert between the
two. Specifically, we assume $G$ to be proportional to the defects transmission $T_d$, an energy-
dependent function, when the tip is near a defect. Contours of constant $G$ denote contours
of constant $T_d(V_{\text{defect}})$ and, if $T_d$ is a smooth function of $V_{\text{defect}}$, they can be interpreted as
contours of constant $V_{\text{defect}}$ without knowing the precise functional form of $G_{\text{defect}}$.

Two aspects of the data in Fig. 6.1 illustrate this argument. First, contours of constant
$V_{\text{defect}}$ must form circles around a defect site in a conventional SGM image, as seen in Fig.
6.1(a). Second, the same contours must follow the curve of Eq. (6.2) in the $\Delta x - V_{\text{tip}}$ plane of
a SGS image. To highlight the agreement of the data with Eq. (6.2), Fig. 6.2(c) reproduces
just the defect region from Fig. 6.1(d), and Fig. 6.2(d) shows an example set of contours
overlaid on the data, with contours of constant $G$ curving through the $\Delta x - V_{\text{tip}}$ plane.

Extracting multiple contours from the data and fitting them to Eq. (6.2) determines the
capacitance $C_{\text{tip}} - bg$ with no free parameters, allowing each contour to be assigned a definite
$V_{\text{defect}}$ value. The lines chosen in Fig. 6.2(d) are evenly spaced from $V_{\text{defect}} = -0.3 \pm 0.3$ V at
intervals of 0.1 V. The proportionality factor $V_{\text{defect}}/V_{\text{tip}}$ ranges from 0.08 – 0.22 for typical
SGS operating conditions. Thus, by explicitly measuring $G(\Delta x, V_{\text{tip}})$, the SGS technique
achieves a significant result: a direct and calibrated conversion of the experimental bias $V_{\text{tip}}$
into the local potential $V_{\text{defect}}$ responsible for the added resistance, without assuming any
particular model function for $T_d(V_{\text{defect}})$.

This fitting process clarifies the size and shape of features in SGS images. When the probe tip
is centered directly over a defect site, the $G(V_{\text{tip}})$ response is extremal. Attenuated responses
away from the defect determine the system capacitance and allow $V_{\text{tip}}$ to be converted into
$V_{\text{defect}}$. Otherwise, the nonextremal $G(V_{\text{tip}})$ values contain no new information about the
defect’s nature or scattering, and certainly do not reflect the physical size of the defect itself.
In fact, the defect position and size are best determined by the residual errors obtained
from fitting contours to Eq. (6.2). The feature in Fig. 6.2(c) appears 450 nm wide, but a
single, simultaneous fit to the multiple contours in Fig. 6.2(d) determines the defect position
to within 15 nm. Within this resolution limit, the defect is indistinguishable from a point scatterer.

The extremal $G(V_{\text{tip}})$ response at the defect position fully describes a defect’s transmission, at least for particular biases $V_{sd}$ and $V_{bg}$. To illustrate this point, Fig. 6.2(e) shows an SGS image with three distinct local maxima in $G(V_{\text{tip}})$. Average $G(V_{\text{tip}})$ values around $x = 2.4 \mu\text{m}$ were extracted and used with Eq. (2) to simulate an SGS image in Fig. 6.2(f). The simulation and raw data agree very well, even though the particular shape of $G(V_{\text{tip}})$ is complex. The example shows that the contours are wholly insensitive to defect identity and that, once $C_{\text{tip}-\text{bg}}$ has been determined, a single curve of $G(V_{\text{defect}})$ extracted at an extremal value is sufficient to describe the defect’s electronic properties. This conclusion simplifies our comparisons in Sec. 6.3.3 of defects having different chemistries.

Finally, application of the Landauer-Büttiker model [29] allows $G(V_{\text{defect}})$ to be converted into an energy-dependent transmission coefficient $T_d(V_{\text{defect}})$. In the strong scattering limit, the two are simply proportional, but the maximum value of $T_d$ depends sensitively on the rest of the device. Before point functionalization, the SWNT and its Schottky barriers can be treated as a single, lumped element $G_{\text{pristine}}$. After point functionalization, $G_{\text{pristine}}$ is in series with the defect contribution $G(V_{\text{defect}})$. By taking advantage of measurements performed on the same SWNT device before and after defect incorporation, we calculate $T_d$ by separating out the $G_{\text{pristine}}$ contribution,

$$T_d^{-1} = 1 + G_0 \frac{G_{\text{pristine}} - G}{G_{\text{pristine}} G} \quad (6.3)$$

where $G_0 = 4e^2/h$ for a SWNT. Unfortunately, relatively high Schottky barriers or other contact resistances in these devices give $G_{\text{pristine}}/G_0$ values that are typically in the range
of 0.5 – 5 %. This low transmission by the contacts limits our ability to clearly resolve very small changes in $T_d$ caused by the defect. At room temperature, for example, $(G_{\text{pristine}} - G)$ often approaches zero, so that the defect transmission is definitely higher than the contact transmission but not necessarily approaching unity. Fortunately, measurements at 130 K always show a substantial difference $(G_{\text{pristine}} - G)$, so that the maximum value of $T_d$ is well defined by the SGS data considered here.

### 6.3.3 Comparison among electrolytes

Data for representative SWNT devices oxidized in H$_2$O, H$_2$SO$_4$, and HCl are shown in Fig. 6.3. For each electrolyte, the portion of an SGS image centered around a defect and an extremal $G(V_{\text{tip}})$ curve extracted from the image are both shown. On the right hand side of the image, a calculated $T_d(V_{\text{tip}})$ curve is shown. Using the capacitance $C_{\text{tip–bg}}$ derived from each image, $V_{\text{tip}}$ is also converted into a local potential $V_{\text{defect}}$.

Figure 6.3(a) depicts the simplest possible type of defect barrier, and it is typical of that observed after point oxidation in H$_2$O. The SGS image shows a high-$G$ channel for $-1 < V_{\text{tip}} < 0$ V, in which the defect transmission peaks at $V_{\text{defect}} = 0$. When gated away from this ideal value, the defect state is no longer resonant and $G$ decreases. This particular data set was analyzed in detail previously [69] using the assumption that $T_d$ approached unity, but a more realistic assessment of the maximum transmission is shown here. We interpret the asymmetry in $V_{\text{tip}}$ to arise from the difference between an attractive and repulsive defect state. For $V_{\text{tip}} > 0$, $V_{\text{defect}}$ lies above the conduction band and it is repulsive (to electron carriers). For $V_{\text{tip}} < 0$, $V_{\text{defect}}$ becomes an attractive trap state that may contribute to tunneling inelastically. A modest oscillation in $G$ on the attractive side suggests the presence of a second state below $-4$ V.

Figure 6.3(b) depicts a barrier resulting from oxidation of an m-SWNT in H$_2$SO$_4$. The
Figure 6.3: Characteristic data for s-SWNTs point functionalized in (a) H$_2$O, (b) H$_2$SO$_4$, and (c) HCl. Each depicts a portion of an SGS data set surrounding the defect site, the maximal $G(V_{tip})$ measured directly over the defect, and a transmission function $T(E)$ calculated from $G(V_{tip})$ and the contact resistance, as described in the text.

barriers formed by H$_2$SO$_4$ or H$_2$O oxidation both have similar, high transmission at $V_{\text{defect}} = 0$, but otherwise the SGS images can be characterized by qualitatively distinct features. First, the $G(V_{tip})$ curve for an H$_2$SO$_4$ defect is much more asymmetric than the H$_2$O case, being
nearly flat for $V_{\text{defect}} > 0$ and much steeper for $V_{\text{defect}} < 0$. The range of $V_{\text{tip}}$ in Fig. 6.3(b) extends over a wider range than in Fig. 6.3(a), in order to resolve what is otherwise a very modest decline in $G(V_{\text{tip}})$ at positive bias. A second qualitative difference is a conspicuous ring of low $G$ in the $\text{H}_2\text{SO}_4$ SGS image. This ring feature stands out particularly well because the $G(V_{\text{tip}})$ minimum is deep and bounded by maxima on both sides. On the $V_{\text{defect}}$ axis, the minimum occurs at $-0.13$ V and the second maximum is at $-0.19$ V.

Figure 6.3(c) continues the sequence with even more pronounced features. In this third example, a defect created by HCl oxidation again results in an asymmetric $G(V_{\text{tip}})$, with $G(V_{\text{tip}})$ nearly constant for all $V_{\text{defect}} < 0$. On the positive side of the $V_{\text{defect}}$ axis, three oscillations of $G$ maxima and minima are observed. The multiple maxima define a series of energies at which $T_d$ is enhanced, suggesting multiple electronic states with an energy spacing of 0.2 eV. As a point of reference, 0.2 eV corresponds to the energy separation of SWNT carriers when confined within a 2 nm quantum dot [12], suggesting a very reasonable length scale for the defect site.

The similarities in the $T_d(V_{\text{defect}})$ curves in Figs. 6.3(b) and 6.3(c) are striking if one accounts for the reversal in polarity. The curves share all of the same features, at least over the range where the experiments overlap. The values of $|V_{\text{defect}}|$ at the first minimum and second maximum are nearly equal in the two cases. Apparently, the bias range that has the least effect on an $\text{H}_2\text{SO}_4$ defect results in the largest oscillations on the HCl defect, and vice versa. Both examples involve m-SWNTs, so the difference is not simply due to n-type carriers versus p-type ones. Instead, we suspect that the defects may incorporate fixed charges due to electron affinities of the attached chemical groups, and that fixed charges having opposite signs could respond to the same $V_{\text{tip}}$ bias with opposite polarities. Further evidence for defect charging is discussed in Sec. 6.3.4.

Additional, quantitative comparison of the three $T_d(V_{\text{defect}})$ curves can compare peak width, peak spacing, and the varying ranges of gate-independent $G$. The HCl oxidation resulted in
narrow peaks suggestive of resonant tunneling through localized, molecule-like states. Interpreting such features will be the first step towards developing a fingerprint of the electronic effects of chemically distinct defects. However, further quantitative analysis or first principles modeling risks over interpretation of the current experimental results. Even though the qualitative differences highlighted in Fig. 6.3 have been established using measurements on multiple devices, the specific patterns of peaks and other unique features vary from sample to sample. Variation in the oxidation process, for example, can lead to over oxidation, spatially extended defects, and a broadening of $T_d(V_{\text{defect}})$ curves that is entirely independent of the electrolyte chemistry. The following two sections focus on this variability and also a bistability that complicates many experiments.

### 6.3.4 Bistability of defect sites

Entirely separate from the features described above, another substantial difference occurs in the stability of the three types of defects studied. At room temperature, defects add conductance noise, and this contribution presumably reflects the defects’ electronic or chemical internal degrees of freedom interacting with the SWNT current. Defect-induced noise is normally quenched upon cooling devices, but of course the internal degrees of freedom remain and can be excited by the scanning probe. This section describes bistability observed during SGS imaging that proves to depend on the electrolyte used during point functionalization.

Figure 6.4 illustrates bistability in the H$_2$SO$_4$-oxidized device discussed previously in Fig. 6.3(b). At 130 K, this m-SWNT exhibits two, readily distinguishable $G(V_{bg})$ characteristics shown in Fig. 6.4(a). In one state (red curve), $G$ is relatively flat for $V_{bg} > 0$ and has a strong dip at $V_{bg} = -4$ V. The second state (blue) has nearly the opposite behavior, being flat except for a strong dip at $V_{bg} = 5$ V. For each state, two $G(V_{bg})$ curves are shown corresponding to positive and negative $V_{sd}$, indicating that the effect is not a simple nonlinearity. SGS can be
performed in either of the two states, with the result that the same SWNT device produces two different SGS images. In the first state, a decrease in $G$ is observed around a defect at $\Delta x = 0.6 \, \mu\text{m}$ for $V_{\text{tip}} < -2 \, \text{V}$ [see Fig. 6.4(b)]. In the second state, a similar decrease is observed but for $V_{\text{tip}} > 2 \, \text{V}$ [see Fig. 6.4(c)]. Good agreement of the SGS images with the $G(V_{bg})$ curves, and the concentration of the gate response around the defect site, are both consistent with the fact that the SWNT was semimetallic before point functionalization.

Figure 6.4: Characteristic data for s-SWNTs point functionalized in (a) H$_2$O, (b) H$_2$SO$_4$, and (c) HCl. Each depicts a portion of an SGS data set surrounding the defect site, the maximal $G(V_{\text{tip}})$ measured directly over the defect, and a transmission function $T(E)$ calculated from $G(V_{\text{tip}})$ and the contact resistance, as described in the text.
Testing has proven that the change from one state to the other is highly reversible and can be induced by the repeated passage of the tip over the defect site at certain $V_{tip}$ values. For example, scanning the tip over the defect site at a bias $V_{tip} > 8$ V is likely to drive the device into the state depicted by Fig. 6.4(c). If the bias is reduced to $V_{tip} < 2$ V, then it can induce a switch to the state in Fig. 6.4(b). Switching is never caused by changes to $V_{bg}$ or by remote tip motion far from the defect site, so we do not believe the effect is due to tip contamination or tip jumping [150]. The bistability is especially problematic for stable SGS imaging, since each image involves multiple ramps of $V_{tip}$ directly over the defect site. Images can be reliably acquired using a limited bias range, but over larger ranges the tip directly perturbs the defect site during image acquisition. Fig. 6.4(d) shows an example of this, with the SWNT flipping from the first state to its second in the middle of the image, as the probe tip traverses the defect position.

These observations all suggest an electrostatic variability localized at the defect site. Charge injection could easily change the sign of a partially charged adduct (i.e., from $+0.5$ to $-0.5$e), but a field-induced rearrangement of the defect chemistry is also a possibility. Either way, the mirror symmetry in the $G(V_{bg})$ curves and SGS images suggests that the gating has opposite effects upon the two states. The energy level of a defect site alternately charged with $+q$ and $-q$ could certainly respond to gating in two opposite directions, but exactly how this charge modulates $G$ remains unclear. Additional experiments, coupled with theoretical modeling, are necessary to establish a better understanding of the mechanism involved.

Despite uncertainty in the mechanism, experiments prove that this bistability is a useful way to discriminate among different types of defects. The behaviors described above are consistent attributes of $\text{H}_2\text{SO}_4$ defects and have been observed in more than 10 devices (though the manifestation is more difficult to observe in p-type s-SWNTs, than in m-SWNTs, because in the former $G(V_{bg})$ drops to zero for $V_{bg} > 0$ V). $\text{H}_2\text{O}$ defects, on the other hand, exhibit a qualitatively different $G(V_{bg})$ bistability, and HCl defects exhibit almost none at
all. Separate transport and noise measurements in the HCl case suggest that tip-charging effects still exist, but with relaxation pathways that are too fast to affect SGS imaging.

SWNT devices point functionalized in H$_2$O, and especially those with multiple defects, exhibit many of the same bistable characteristics as the H$_2$SO$_4$ case described above. However, the modest $V_{bg}$ sensitivity of H$_2$SO$_4$ defects is replaced by much stronger gate dependence in the H$_2$O case. Figure 6.5(a) shows the two possible $G(V_{bg})$ characteristics for a m-SWNT device point functionalized in H$_2$O. In one state (red curve), $G$ is predominantly p type, while in the second state (blue curve) it is n type. Note that $G$ is plotted on a logarithmic scale.

Figure 6.5: (a) A defect produced in H$_2$O results in two dissimilar $G(V_{bg})$ behaviors that are predominantly p or n type. (b) A single SGS image from the same device, capturing switching between the two states as the tip traverses the defect site. Defects produced in H$_2$O prove to be the most difficult to image, even when acquired using modest $V_{tip}$ ranges.

Another difference between H$_2$SO$_4$ and H$_2$O defects is that the latter type switches much more predictably. At modest biases $|V_{tip}| > 3$ V, over 90% of tip traverses change the state
of H$_2$O-oxidized SWNTs. Switching can also be induced by setting $|V_{bg}| > 5$ V. As a result of this sensitivity, SGS images like Fig. 6.3(a) are unusually difficult to obtain around H$_2$O defect sites. Fig. 6.5(b) is a more typical SGS image corresponding to the curves in Fig. 6.5(a). In this example, the device begins in its p-type state, but then transitions from the p-type state to the n-type state and back on every pass of the tip from $\Delta x = 1.4 \mu$m up to $\Delta x = 1.5 \mu$m. Because the switching occurs at progressively larger $V_{tip}$ values on each pass, the transition in the SGS image appears slanted in the $\Delta x - V_{tip}$ plane. The smoothness of the transition illustrates the reliability of the switching, and further suggests that the energetic barrier pinning the defect into one state or the other can be continuously varied by $V_{tip}$. Images having the opposite contrast can be obtained by setting $V_{bg} > 5$ V so that the device begins in the n-type state.

Even though the $G(V_{bg})$ behaviors in Figs. 6.4(a) and 6.5(a) are very different for the two electrolytes, both are consistent with the charge injection model proposed above. In the first case of H$_2$SO$_4$, the weak scattering means that charging the defect has only a modest effect. In the second case of H$_2$O, the same degree of charging has an effect amplified by the very deep minimum in $G(V_{bg})$. A positively-charged defect site blocks p-type carriers more strongly than n-type carriers, and a negatively-charged defect does the opposite. Thus, charge injection from the tip to the defective region gives the device a persistent memory that selects for one type of carrier over the other. The low-conductance feature at $V_{bg} = -2$ V in Fig. 6.5(a) is intriguing because it is seven times more conductive in one state than the other, but further study is necessary to determine whether such features are common among different devices.
6.3.5 Variation in the degree of SWNT oxidation

Ideally, point functionalization is performed near the threshold of oxidation where individual, covalent events are stochastically separated in time. Under those conditions, sharp, discrete drops in $G(t)$ indicate the covalent addition of individual point defects. Reproducible point defects are prerequisite for the defect-to-defect comparison described above. However, two variations in the point functionalization process are common, and both result in more extensive oxidation and complexity that prevents reliable and reproducible analysis. This section discusses these variations and the SGS images that result.

First, consider the case of optimum point functionalization. In Fig. 6.6(a), point functionalization proceeds as desired, with a pair of sharp drops occurring within $\Delta t = 0.1$ s and leaving $G(t)$ in a low conductance state. Upon electrochemical reduction, devices returned nearly all the way to $G_{\text{pristine}}$. Defects incorporated in this manner were rarely evident in room temperature $G(V_{bg})$ measurements except at specific values of $V_{bg}$, justifying the discussion of high transparency in Sec. 6.3.2. These properties are also consistent with the premise of single defect incorporation, so they have been used as criteria for selecting images here and in previous reports [54, 69].

Figure 6.6(b) depicts a common example of point functionalization that does not proceed in the desired sequence. Electrochemical oxidation is not halted after the initial step or series of steps in $G(t)$ because the transitions do not decrease monotonically. Instead, bistable switching in $G(t)$ persists for one or more seconds. The metastable, rapidly switching intermediate levels are believed to reflect competition between covalent and noncovalent configurations of ions interacting with the SWNT sidewall [85], and may also indicate the creation and spatial reorganization of multiple defects clustered together [7]. After oxidation along the lines of Fig. 6.6(b) and subsequent chemical reduction, SWNTs recover just $20 - 80 \%$ of $G_{\text{pristine}}$. Substantial new $V_{bg}$ dependence is observed at room temperature, indicating $T_d$
Figure 6.6: Variability of point functionalization in HCl for three SWNT devices. (a) One or two discrete drops in conductance occurring in $\Delta t < 1$ s indicates the most likely creation of a covalent point defect. (b) Multiple drops with bistable dynamics over a few seconds suggests more complex damage, such as the creation and clustering of multiple sites. (c) A continuous decrease over many seconds indicates extensive and irreversible oxidation. In all three examples, individual data points correspond to 50 kHz sampling rate. Insets show example SGS images for the less ideal cases.

values comparable to the contact resistance. At lower temperatures, $T_d$ becomes much less than 1 % and adopts complex gate dependences. These properties result in SGS images that
are not immediately distinguishable from those in Figs. 6.1-6.3, but which upon analysis have features that are unique to a particular device. An example is shown in the inset to Fig. 6.6(b). The greater complexity of these compound defects prevents reliable and reproducible analysis.

A third type of oxidation is also possible in which no discrete changes are observed at all. Fig. 6.6(c) depicts an example in which $G(t)$ decreases to zero continuously and smoothly over the course of 40 s. Devices that oxidize in this manner may not conduct at all after chemical reduction, and those which do only recover a small fraction of $G_{\text{pristine}}$. Both cases indicate a greater degree of oxidation, almost certainly extending over multiple sidewall sites. In fact, a similar type of spatially extended oxidation has been directly imaged by electron microscopy [191]. Of those devices which do conduct, SGS imaging usually reveals a relatively simple and one-sided $G(V_{\text{tip}})$ that is featureless at one polarity and exponentially and monotonically decreasing at the opposite polarity. An example SGS image is shown in the inset to Fig. 6.6(c). First-principles calculations have calculated the transmission of multiple clustered defects in different arrangements, but a multitude of possible arrangements limits any meaningful comparisons with experiment. Because the degree of experimental damage is impossible to verify in these cases, attention has instead focused on the simplest types of oxidation represented by Fig. 6.6(a).

All three types of $G(t)$ oxidation sequences are possible in SWNT devices, even using the same electrolyte. For instance, all three examples in Fig. 6.6 are obtained using HCl. In either HCl or H$_2$O, only 2 out of 10 device oxidations produced traces like the one shown in Fig. 6.6(a). This success rate, albeit limited, was sufficient to allow the comparative SGS analysis done in Fig. 6.3. The majority of the oxidations proceeded smoothly as in Fig. 6.6(c). Accordingly, the original report on point functionalization identified H$_2$O, HCl, and NaOH as the poorest candidates for successful point functionalization because of their unreliable production of discrete oxidation and/or reduction steps in $G(t)$ [54]. On the other
hand, $G(t)$ traces like Figs. 6.6(a) or 6.6(b) occur with a 90% probability when point functionalization is performed in H$_2$SO$_4$ or HNO$_3$. This high success rate makes the production of point defects relatively straightforward in these acids. Nevertheless, the remaining possibility of a nonideal oxidation as in Fig. 6.6(b), combined with the metastable switching described in Sec. 6.3.4, conspire to make SGS imaging time consuming and difficult to analyze even in this case.

### 6.4 Conclusion

To summarize, successful point functionalization introduced scattering sites that were quantitatively probed by the SGS technique. Functionalization in three different electrolytes resulted in defect sites exhibiting clearly distinguishable characteristics. All three types of defects responded to gating with a dominant transmission maximum, but the conductance on either side of this peak was electrolyte dependent. Oxidation in H$_2$O produced the most symmetric response, with $G$ substantially reduced on either side of the transmission peak. H$_2$SO$_4$ and HCl oxidations both produced more asymmetric characteristics that were substantially transparent at one polarity and contained one or more transmission minima at the other polarity. H$_2$SO$_4$ oxidation produced a single transmission minimum that resulted in distinctive SGS images. HCl oxidation, on the other hand, produced a series of multiple, shallower minima.

The stability and reproducibility of a given SGS image was also found to be dependent on the electrolyte used. H$_2$O defects reliably switched between two states having dissimilar conductances. H$_2$SO$_4$ defects also exhibited two distinct states, but they were less different in conductance and metastable or longer-lived in the presence of a biased tip. HCl defects had a very transient bistability that was difficult to characterize, but which resulted in the most stable imaging conditions of the three.
In all three electrolytes, the observed transmission curves were interpreted in terms of differences in the underlying electronic structure of defect state, but the analysis in this direction remains preliminary. The experimental data provide the impetus for further measurements, to be combined with first principles modeling of these effects.
Chapter 7

One-dimensional Poole-Frenkel conduction in the single defect limit

A single point defect surrounded on either side by quasi-ballistic, semi-metallic carbon nanotube is a nearly ideal system for investigating disorder in one-dimensional (1D) conductors and comparing experiment to theory. Here, individual single-walled nanotubes (SWNTs) are investigated before and after the incorporation of single point defects. Transport and local Kelvin Probe force microscopy (KPFM) independently demonstrate high-resistance depletion regions over 1.0 \( \mu \text{m} \) wide surrounding one point defect in semimetallic SWNTs. Transport measurements show that conductance through such wide depletion regions occurs via a modified, 1D version of Poole-Frenkel field-assisted emission. Given the breadth of theory dedicated to the possible effects of disorder in 1D systems, it is surprising that a Poole-Frenkel mechanism appears to describe defect scattering and resistance in this semimetallic system.\(^1\)

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7.1 Introduction

A single point defect can convert a ballistic, one-dimensional (1D) conductor into a highly resistive wire, [14, 41, 83, 8, 174] and a pair of defects can produce Coulomb blockade effects as high as room temperature [145]. Driven by these dramatic effects, the current International Technology Roadmap for Semiconductors [22] calls for physics models to better address the role of single defects and dopants in semi-classical 1D devices. Unfortunately, well-characterized systems for studying defect-induced effects is acknowledged as a challenging gap to address experimentally [93]. Theory predicts a range of novel quantum phenomena with practical consequences in disordered 1D conductors [98, 165, 53, 177, 34, 35, 67, 6] such as resistivity dipoles and Luttinger scaling exponents. Experiments, however, are often limited to random contaminants and imperfections of unknown character. The precision placement of individual atoms into conducting structures, either using scanning probe tips [45] or by implantation [174, 159], is a notable example for which quantum transport has been studied at cryogenic temperatures, but these quantum states are not robust at higher temperatures.

Single-walled carbon nanotubes (SWNTs), on the other hand, exhibit a quantum mechanical regime extending to room temperature [31] and hints of Luttinger liquid behaviors above 100 K [31, 13, 72]. In past work, SWNTs have been a poor example of precision control: disorder in SWNTs has been ubiquitous, random, and varied [9, 41, 83, 181]. Recently, we demonstrated an electrochemical technique for adding a single oxidative adduct to SWNT transistor devices [54]. These oxidized defect sites were sufficiently disruptive to affect SWNT conductance at room temperature, and in relatively clean SWNT devices (those exhibiting room-temperature inelastic mean free paths > 1µm), they could be the sole inelastic scattering site. Here, we report measurements comparing individual SWNTs before and after defect incorporation and show that these sites fail to demonstrate the power-law scaling of a Luttinger liquid or the activated thermodynamics of a simple barrier. Instead, defect
scattering in SWNTs has the temperature and bias dependence of Poole-Frenkel conduction, though with modifications accounting for the 1D electrostatics. The Poole-Frenkel mechanism, which is normally applied to thin, 2D insulators [44, 162, 161], has never been observed in the limit of a single defect, and its applicability to point defect scattering in a 1D channel is wholly unanticipated in the theoretical literature. Some past research has reported Poole-Frenkel conduction in SWNTs [115, 79, 113, 139, 140, 154, 153], but it has always been attributed to ensemble disorder.

7.2 Experimental Methods

Figure 7.1(a) depicts a schematic of the device layout, with the p++ Si serving as a back gate electrode. Electronic characterization of the source-drain current ($I_D$) as a function of drain and gate biases ($V_D$ and $V_G$) identified quasimetallic samples (m-SWNTs) with modest $V_G$ sensitivity that were the primary focus of this investigation.

Single point defects were introduced into each SWNT using the method of conductance-controlled point functionalization [54, 25]. Briefly, this method uses $I_D(t)$ as a real-time indicator of covalent modifications during the dilute electrochemical oxidation of a SWNT device [54, 115]. The oxidation, which is believed to be the covalent addition of an $-\text{OH}$ adduct, was precisely limited to a single stepped drop in $I_D(t)$ defect using a software trigger with a 30 ms response time that dropped the oxidative potential down to 0 V. In this manner, single defects were achieved in 80 % of attempts and further oxidative damage was strictly limited. Figure 7.1 shows a typical $I_D(t)$ trace in which a device increased resistance from 430 to 600 kΩ in one discrete step while being held near the threshold for electrochemical oxidation in water. Oxidation occurred at a random position along each SWNT channel, then the sites were subsequently located by scanning-probe imaging [54].
Figure 7.1: Carbon nanotubes with single point defects. (a) Three-terminal and scanning probe characterization of a m-SWNT. (b) Example drop in $I_D$ used to identify point-defect incorporation by electrochemical oxidation. (c) $I_D(V_G)$ before and after defect incorporation, with (d) SGM image of the localized nature of the new gate dependence. (e) $I_D(V_D)$ at $V_G = -1$ V before and after defect incorporation, and (f) corresponding KPFM image illustrating the large potential gradient at the same site. All data acquired at $T = 180$ K.

To precisely determine the electronic effects of a defect, each SWNT was characterized before and after this electrochemical defect incorporation. After oxidation, devices were immediately blown dry and transferred into a high-vacuum ($10^{-7}$ Torr), variable-temperature transport and AFM system (JEOL JSPM 5200) was used to acquire $I_D(V_D, V_G, T)$ and surface maps of local properties. Frequency-modulated Kelvin Probe Force Microscopy (KPFM) was used to image surface potentials $V_{KP}$ and potential gradients resulting from scattering [121] using a custom-designed KPFM system that has been described previously [50, 49]. Scanning gate microscopy (SGM) was also used to locate the defects based on their localized gate sensitivity $dI/dV_G$ [168, 69, 68]. Images shown here were all acquired at 185 K to eliminate
hysteresis and drift associated with mobile surface contaminates at higher temperatures. In our system, custom electronics synchronized AFM imaging to the acquisition of $I_D$ and control of $V_D$, $V_G$, and the probe tip potential $V_T$. In this work, the lateral KPFM resolution was limited to $20 - 50$ nm by the probe tip diameter [50]. This resolution was at least ten times narrower than the average potential gradients analyzed below, so tip resolution does not affect the conclusions drawn.

### 7.3 Results

Figure 7.1 illustrates the increases of resistance and gate sensitivity that accompanied the addition of a defect to an example m-SWNT. Compared to the pristine case before modification, the damaged m-SWNT exhibited a higher low-bias resistance, a non-Ohmic $I_D(V_D)$, and twice as much gate modulation in $I_D(V_G)$ (Figures 7.1c and 7.1e), all in accord with previous reports [54, 36]. Scanning probe imaging further proved these effects to be localized. Figure 7.1d shows an SGM image of $dI/dV_G$ (red) overlaid on AFM topography (grey), indicating how the increased gate sensitivity in Figure 7.1c was entirely concentrated at one spot midway between the source and drain connections. Figure 7.1f shows that KPFM imaging of $V_{KP}$ under similar conditions ($V_G = -1$V) resolved a large potential drop at the same location. In comparison, pristine m-SWNTs exhibited shallow KPFM potential gradients with large drops at the electrode interfaces [50, 49] and minimal SGM sensitivity [30,32].

Data from other SWNTs showed qualitatively similar features to Figure 7.1. Semiconducting SWNTs, which have intrinsic gate responses and Schottky barrier effects [122, 168, 120], have been excluded from this report in favor of the simpler characteristics of m-SWNTs, which are more straightforward to interpret.

Two experimental methods were used to investigate the added resistance associated with point defects. Higher-resolution KPFM versus $V_D$ and $I_D$ allowed for a detailed investigation
of the potential gradients surrounding a scattering site. Figure 7.2a shows a set of KPFM images acquired from the device of Figure 7.1 as it was biased from +2.0 to -2.0 V in 0.5 V increments (from left to right, with $V_D = 0$ not shown). Exchanging the role of source and drain produced the most intuitive and directly comparable images of reverse polarity, so that technique has been used here. These images have been cropped to highlight the region surrounding the SWNT defect, and line cuts along the SWNT channel (Figure 7.2b) were extracted for analysis. At the locus of SGM sensitivity, KPFM resolved a small potential barrier at $V_D = 0$ (Figure 7.2b, bottom) and a symmetric, high-field potential drop $F = dV_{KP}/dx$ in response to currents (Figure 7.2b, top). For example, at $V_D = 1$ V, the KPFM potential drop $\Delta V_{KP}$ was $0.68 \pm 0.04$ V and the field reached $F = 0.76$ V/µm. This drop in potential corresponded to a local resistance $\Delta V_{KP}/I_D = 928 \pm 54$ kΩ that was two-thirds of the total device resistance and that matched the two-terminal increase measured at the same temperature and bias. In this manner, KPFM allowed direct measurements of each defect’s resistance, independent of contact resistances and diffusive scattering along the rest of the SWNT. Diffusive scattering far from defect sites has been extensively investigated at low and high bias by transport techniques [18, 42, 18] and by quantitative KPFM [50, 49], so it is not the focus of this report.

To complement direct KPFM imaging, two-terminal measurements of $I_D(V_D, V_G, T)$ were acquired over a wider range of bias and temperature. Figure 7.2c shows an example measurement of $I_D(V_D)$ at $T = 77$ K plotted on axes used for Poole-Frenkel (PF) analysis. The pristine SWNT had an ohmic, temperature-independent conductance that resulted in a nearly-horizontal line on these axes; the addition of a defect reduced the conductance and induced a non-ohmic bias dependence. The PF axes are clearly inappropriate for the raw data, which unlike KPFM include the contact resistance and diffusive channel contributions. However, careful subtraction of $I_D(V_D)$ data sets before and after defect incorporation allowed us to define the additional drain voltage $\Delta V_D$ necessary to obtain a particular current $I_D$ at fixed $V_G$ and $T$. This subtraction approximates the semi-classical limit of the
Figure 7.2: (a) Selected portions of KPFM images around a m-SWNT defect site at $V_D = +2$ to $-2$ V in 0.5 V steps. (b) KPFM line cuts extracted along the m-SWNT, with reverse-bias data plotted as dashed lines. (c) Example Poole-Frenkel plots of raw data $I_D(V_D)$ at $T + 77$ K before and after defect incorporation. (d) Poole-Frenkel plot of the differential, added resistance $I_D(V_D, T)$, with fits to Eq. 7.1 (dashed lines).

Landauer-Buttiker formalism, in which each constituent scattering mechanism constitutes a series resistance. So long as point functionalization occurs far from the electrodes and does not affect the SWNT’s contact resistance or inelastic mean free path, the addition of one new scattering site introduces an extra voltage drop $\Delta V_D$ for a given $I_D$. A similar distinction between $I_D(V_D)$ and $I_D(V_D)$ can be used to analyze ensemble radiation damage [167].
7.4 Discussion

The $I_D(V_D)$ difference curves suggested bias increases $\Delta V_D$ that were in excellent agreement with the potential drops $\Delta V_{KP}$ measured directly by KPFM. Furthermore, these curves fit the functional form of Poole-Frenkel (PF) conduction over a wide range of bias and temperature. PF conduction is governed by

$$I_D(\Delta V_D, T) = a\Delta V_D \exp\left[-q(\Phi_0 - b F^{1/2})/k_B T\right]$$  \hspace{1cm} (7.1)

where the detrapping electric field $F$ is proportional to $\Delta V_D$ and $a$ and $b$ are both positive constants [22,39]. PF fitting for $I_D(V_D)$ curves at six temperatures is shown in Figure 7.2d. Plots of $\ln(I_D/\Delta V_D)$ versus $\Delta V_D^{1/2}/T$ at different temperatures produced a family of nearly parallel, straight-line curves for each m-SWNT we have investigated.

The PF model is most frequently used to predict the enhanced transport that occurs when localized defect states enhance conduction through thin, insulating films [161, 173]. The unbiased and biased situations are depicted by energy diagrams in Figure 7.3a. Each defect is modeled as a Coulomb trap with a barrier $\Phi_0$ in an insulating film of thickness $D$ and dielectric constant $\epsilon$. When the insulator is biased, charges may tunnel into this trapping state and then be emitted into the insulator’s conduction band. The PF mechanism describes this emission: the mean applied field $F = \Delta V_D/\epsilon D$ lowers the barrier from $\Phi_0$ to $\Phi$ by an amount proportional to $F^{1/2}$ [162, 166], leading to the functional form expressed in Eq. 7.1. PF plots like the one shown in Figure 7.2d can be used to extract experimental values of $\Phi_0$ [166, 186] that are typically 1 to 2 eV for traps in SiO$_2$.

Fitting Eq. 7.1 to SWNT data results in inferred barrier heights $\Phi_0$ of only 10 to 40 meV and small detrapping fields $F$, the latter of which suggest effective lengths $D = \Delta V_D/\epsilon F$ approaching the 2 $\mu$m source-drain separation. Such small barriers and wide lengths were
Figure 7.3: Energy band diagrams compare Poole-Frenkel conduction through a 2D insulator and through the depletion region surrounding a SWNT defect. In both cases, the insulating region has a characteristic dimension $D$, a defect-induced trap state (red), and an effective barrier height $\Phi < \Phi_0$. $\Phi$ is on the order of 1 eV for a conventional insulator but only $10^{-50}$ meV for the small band gap of a m-SWNT. $E_F$ is the Fermi energy of carriers.

discounted as unphysical in the first report of PF conduction in SWNTs [115], but subsequent researchers have repeatedly shown that highly disordered and damaged SWNT films can all be fit to Eq. 7.1 [79, 113, 140, 139, 154, 153] The application of Eq. 7.1 to point disorder in 1D m-SWNTs is not self-evident because the electrostatics of the PF mechanism across 2D insulators and 1D conductors are so dissimilar. Furthermore, detrapping fields $F$ over micron-scale lengths seem inconsistent with the single-defect limit studied here. In 2D insulating films, the PF mechanism can be relevant for insulators up to 300 nm thick, but only because the model can be extended to ensembles of traps having broad energy distributions [166, 186].

Nevertheless, KPFM imaging directly observes fields on the order of 1 V/$\mu$m and potentials $\Delta V_D$ dropping over $\mu$m distances, proving that the lengths inferred from PF fitting are physically relevant. As one example, the PF slopes in Figure 7.2d were observed in KPFM as a high-$F$ region extending for $0.9 \pm 0.1$ $\mu$m. As seen in Figure 7.2b, the width of the high-$F$ region was relatively insensitive to $V_D$ and it extended symmetrically around the defect site. Similar agreement between KPFM and transport has been observed in all
SWNT samples, proving that Eq. 7.1 appropriately captures the bias dependence for single-defect scattering in a SWNT. Furthermore, PF fitting to Eq. 7.1 determines the average field $\Delta V_D/\epsilon D$ and KPFM measurements observe $\Delta V_D$ and $D$, so the two can be combined to solve for $\epsilon$. The resulting value of approximately 2.5 is intermediate between air and SiO$_2$, as is generally assumed for exposed SWNT devices. Previously, authors reporting PF fitting have hypothesized that small fields $F$ were evidence of diffusive scattering due to gross disorder introduced by SWNT processing, entanglement or other materials issues [79, 113, 140, 139, 154, 153]. Here, before-and-after imaging in the single-defect limit proves that $F$ is small because $\Delta V_D$ drops uniformly over substantial widths.

Moreover, experimental agreement between transport and KPFM also covered the strong gate sensitivity shown in Figure 7.1c. Transport data for different m-SWNTs led to detailed sets of $I_D(V_D, V_G, T)$ data, each of which exhibited excellent fits to Eq. 7.1 (0.9<R<1) when the two parameters $\Phi_0(V_G)$ and $D(V_G)$ were allowed to be gate-dependent. Figure 7.4a shows $D(V_G)$ and $\Phi_0(V_G)$ from one m-SWNT, with ± 1 σ error bars to illustrate which features were significant (and assuming a value $\epsilon = 2.5$ intermediate between SiO$_2$ and air). Ignoring fine details, similar features across different devices included sharp extrema, broad regions insensitive to $V_G$, and anticorrelated $\Phi_0$ and $D$. KPFM was too laborious to map the full $V_G$ dependence, but it was used to confirm that high-$F$ regions widened or shortened in response to moderate gating at $V_G = -1$, 0, and +1 V. This direct imaging helped prove that the width of high-$F$ regions like those shown in Figure 7.2b were much more sensitive to $V_G$ than to $V_D$. KPFM also revealed that SWNT diameter played an important role in systematically scaling with width of the high-$F$ regions, which ranged from 0.3 to 0.9 µm for one m-SWNT but from 1.1 to 2.4 µm for another. Figure 7.4b shows KPFM measurements of this apparent width at $V_G = -1$ V from four m-SWNTs, with a fit illustrating the inverse diameter dependence $D = (1.06 \pm 0.01$ nm$)(\text{diameter})^{-1}$. Variability in extrinsic doping among different SWNTs limited a more quantitative comparison, but future work could investigate gate dependence in more detail.
Figure 7.4: (a) Gate dependence of defect-induced barrier width \( D \) and height \( \Phi \) in a 1.6–nm m-SWNT. (b) Comparison of \( D \) among four m-SWNTs, all measured at \( V_G = -1 \) V and confirmed by direct KPFM imaging. Dashed line shows least-squares fit to an inverse diameter law. All error bars are one standard deviation.

Finally, we note that the applicability of Eq. 7.1 was surprisingly insensitive to the extent of chemical disorder. Point-functionalized devices having very modest (\( \approx 10\% \)) increases in room temperature resistance were compared against devices that had been exposed to more extensive electrochemical oxidation, ultimately up to the limit of near-insulating devices analyzed previously [54, 115, 79, 113, 140, 139, 154, 153]. When the differential technique described above was used to isolate \( \Delta V_D \) and analyze only the increase in resistance, all types of damage exhibited a PF bias dependence with apparent barriers a few 10’s of meV high and widths of 0.3 \( \mu m \) or more.

The results described here challenge conventional theoretical treatments of SWNT defect scattering, which have not previously predicted a PF bias dependence or \( \mu m \)-scale high-field regions. We believe the most relevant work is the prediction that point charges near a SWNT can induce carrier depletion over widths exceeding 1 \( \mu m \) [106, 105]. The Coulomb potential of a charged adduct, such as the \(-\text{OH}\) chemical group introduced here, is essentially unscreened.
by the small, 1D carrier density of m-SWNTs. At $V_D = 0$, KPFM around defects directly imaged sharp potential peaks on top of broad shoulders, and we interpret these features as charged defects surrounded by zones of carrier depletion (Figure 7.2b). At $V_D > 0$, the depletion zones result in high-field regions that stay symmetrically centered around the defect but which vastly exceed the defect’s spatial extent. In fact, such long depletion widths appear to be a hallmark of SWNT conduction. At Schottky barrier interfaces, Freitag et. al. used scanning photovoltage imaging to image band bending and depletion widths extending over many microns [43]. SWNT screening lengths are predicted to depend sensitively on SWNT diameter, chirality, and carrier density, with a general trend towards better screening in larger diameter SWNTs [107, 37] due to weaker charge confinement effects [106, 105]. All of these elements are supported by observations described here, though we do not rule out other possible phenomena such as negative quantum capacitance [100, 37].

The applicability of Eq. 7.1 further requires that field-assisted emission from localized states is a key to the conduction observed through these wide depletion regions. A charged adduct and its associated disorder have one or more localized electronic states that may be involved, and we propose that trapping and detrapping by this state is responsible for the successful fitting to Eq. 7.1. Fig. 7.3 illustrates the functional equivalency between the conventional, 2D insulator having a charged trap state (Fig. 7.3a) and the depleted region of a 1D m-SWNT surrounding a charged adduct (Fig. 7.3b). The band bending and depletion in the m-SWNT that are observed by KPFM at zero bias produce a semi-insulating region that plays a role similar to the insulating film; at high-field, charge injection into the SWNT defect state and field-induced emission out of it lead to conduction that mimics the PF behavior of thin films. In addition, the high fields and disorder may hybridize the SWNT subbands or allow mechanisms such as interband Zener tunneling [86] to introduce the necessary states. We note that $\Phi_0$ is comparable to the small band gaps of m-SWNTs [31] and that any model incorporating SWNT subbands would symmetrically accommodate defects having either positive or negative charge. In any case, first-principles modeling will be needed to
determine the exact mechanisms that allow Eq. 7.1 to apply to defect scattering in SWNTs. The conventional interpretation in PF conduction has no explicit dependence on carrier density nor $V_G$, since neither of these has a role in determining $F$ in 2D insulating thin films. Furthermore, trap emission depends exponentially on $F$, which in 1D has unique electrostatics and is sensitive to details of the carrier concentration, confinement effects, and electron correlation [32, 16].

7.5 Conclusion

In conclusion, we directly imaged potential drops surrounding single, isolated SWNT defects and found that the high-field regions could extend to over 1 $\mu$m in length, in agreement with theoretical predictions of divergent depletion lengths in 1D [106]. Conduction through these depletion regions followed a gate-dependent, Poole-Frenkel-like characteristic that challenges existing models of defect resistance. Such long depletion lengths have not been reported in PF-limited semiconductor nanowires [87, 1] or 2D graphene in the low-carrier density limit [188, 187]. As emphasized by Yu et. al. [188], the combination of low carrier densities and a 1D geometry may prove to be critical for understanding not only the effects of defects and disorder but also heterojunctions and contact resistance in extremely scaled semiconductor devices.
Bibliography


Appendices

A The original Jeol JSPM-5200 electronics

Fig. A.1 depicts an overview of the original Jeol JSPM-5200 electronics including the various cables and interconnects for digital and analog signals. The instrument consists of six main components: the SPM, amplifier, lock-in amplifier, SPM controller, temperature controller and personal computer (PC). The cable interconnects between each of the components are labeled (rectangles) so that Fig. A.1 can be used as a guide for assembling the instrument electronics. For each of the instrument cables (dashed lines) the primary type of routed signal has been labeled.

The primary function of the amplifier and controller are illustrated by following the topography feedback loop shown in blue in Fig. A.1. Inside the SPM, AFM or STM electronic signals are sent to a preamp for an initial stage of amplification. The preamp output is then routed through connector FA1 for further amplification and signal processing by the amplifier. The output of the amplifier is then sent to the SPM controller via connector FA-A (AFM) and PR (STM). Inside the controller, the AFM or STM signals are used as inputs to an PID feedback loop. The output of the feedback loop is then amplified to high-voltage and sent to the scanner piezo to control the probe distance from the sample surface.

In addition to operating the instrument feedback loops, the SPM controller also scans the
tip across the sample surface in conjunction with control software on the PC. The control software, Jeol WinSPM 4.0, sends digital signals from the DT-3016 PCI card to the SPM controller via connector DT-D. The controller converts the digital signals to scan voltages that are amplified and sent to the piezo via connector PZT. During scanning, the AFM and STM signals are sent from the controller to the DT-3016 PCI card via connector DT-A for image acquisition.

Figure A.1: Overview of the instrument