Summer 7-26-2017

Properties of Carbon Nanotubes: Defects, Adsorbates, and Gas Sensing

Micah C. Eastman
Portland State University

Follow this and additional works at: https://pdxscholar.library.pdx.edu/open_access_etds

Part of the [Physics Commons](#)

Let us know how access to this document benefits you.

Recommended Citation

Eastman, Micah C., "Properties of Carbon Nanotubes: Defects, Adsorbates, and Gas Sensing" (2017).
Dissertations and Theses. Paper 3775.
<https://doi.org/10.15760/etd.5659>

This Dissertation is brought to you for free and open access. It has been accepted for inclusion in Dissertations and Theses by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.

Properties of Carbon Nanotubes: Defects, Adsorbates, and Gas Sensing

by

Micah C. Eastman

A dissertation submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy
in
Applied Physics

Dissertation Committee:

Jun Jiao, Chair

Bin Jiang

Erik Sanchez

Raj Solanki

Tami Clare

Portland State University

2017

Abstract

Carbon naotubes and graphene have been a trending research topic in the past decade. These graphitic compounds exhibit numerous advantageous properties (electronic, mechanical, thermal, optical, etc) which industry and researchers alike are excited to take advantage of. Beyond the challenges of yield and controlled growth, there are a number of standing questions which govern some of the more fundamental characteristics of these materials: What role do lattice defects play in the adsorption of gas molecules on the surface of carbon nanotubes? How are the electronic states of the carbon nanotubes influenced by these adsorbed molecules? And how can we develop models to predict useful applications of this knowledge?

In order to address these questions, this study combines Raman spectroscopy and electronic measurements carried out in highly controlled environments of carbon nanotube transistors. Assessing these data in conjunction shows that the defect density of a carbon nanotube channel has no correlation with observed threshold voltage shifts, or change in Schottky barrier, due to the presence of ambient oxygen. With these insights in mind, a dynamic adsorption-desorption model is proposed which addresses the oxygen sensitivity of carbon nanotube transistors. Instrumentation and computational developments which facilitated these measurements are also disclosed.

Acknowledgements

I would like to thank my research advisor, Prof. Jun Jiao, for her continued support and guidance over the course of my graduate studies and my thesis committee for their time, interest, and input on my project. I am also thankful of the entire Department of Physics faculty, support staff, and graduate student body for their friendship and kind assistance which always seemed to be in ample supply.

I will always be grateful for the seemingly inexhaustible patience of my wife, Meghann Eastman, who is the greatest companion I could hope to have in life; and for the rest of my family, which has ever been a source of love and levity.

Portions of this work have been supported by Intel Corporation and the National Science Foundation (NSF) under award no. 1057565 and REU site no. 1004737. Financial support for acquisition of instrumentation was also provided in part by the Oregon Nanoscience and Microtechnologies Institute (ONAMI).

Table of Contents

Abstract	i
Acknowledgements	ii
List of Tables	v
List of Figures	vi
List of Abbreviations/Symbols	ix
1 Introduction	1
1.1 Applications of carbon nanotubes	1
1.2 Current literature: Status and limitations	3
1.3 Approach & organization	4
2 Experimental Concepts	8
2.1 Physical and electronic structure of carbon nanotubes	8
2.2 Raman scattering in graphitic compounds	14
2.3 Carbon nanotube field-effect transistors	17
2.4 Charge carrier transport	20
3 Experimental Methods	23
3.1 Quantitative Raman spectroscopy	23
3.2 Polarization-dependent Raman spectroscopy	25
3.3 Electron transport measurements	29
3.4 Electrical impact of adsorbates	30
4 Instrumentation Developments	34
4.1 Raman spectrometer	34
4.1.1 Motorized half-wave plate	35
4.1.2 Quarter-wave plate optics	36
4.2 Micro-environmental probe station	38
4.2.1 Gas injection and sensing	39
5 Computational Methods	42
5.1 Raman region identification	43
5.2 Raman map stitching	45
5.3 Effective Schottky barrier	49

6	Results	53
6.1	Device fabrication	53
6.2	Raman spectroscopy	54
6.2.1	Defect mapping	54
6.2.2	Defect quantification	55
6.3	Electron transport	57
6.4	Correlations	59
7	Discussion	62
7.1	Defect density estimation	62
7.2	Gas-surface collisions	65
7.3	Chemisorption and physisorption processes	66
7.4	Dynamic nanotube-adsorbate model	68
7.5	Charge traps and transport	72
8	Conclusion	74
8.1	Broader impact	76
8.2	Further studies	77
8.2.1	Differentiation: metallic vs. semiconducting	77
8.2.2	Photostimulated transport	78
8.2.3	Kelvin probe measurements	79
	References	80
	Appendix A Python code	85
A.1	Classes	85
A.1.1	CNTFET	85
A.1.2	MEPS	86
A.1.3	GateSweep	89
A.1.4	Raman	93
A.2	Functions	102
A.2.1	Curve fitting	102
A.2.2	Raman map stitching	102
A.3	Code blocks	103
A.3.1	Raman map stitching	104
	Appendix B Publications	108
	Journal Publications	108
	Conference Proceedings	108
	Co-authored Publications	108

List of Tables

Table 1: Collision rates of O ₂ molecules at various pressures with entire CNT channel and with defect sites.	66
---	----

List of Figures

Figure 1: Flow diagram of experimental approach and techniques applied.	5
Figure 2: (a) Unit cell and (b) first Brillouin zone of monolayer graphene	8
Figure 3: (a) Pristine graphitic carbon and (b) monovacancy, (c) divacancy, and (d) Stone-Wales defects	9
Figure 4: Schematic of 2D basis for CNTs with chirality boundary points labeled. Red indicates semiconducting chiralities, and blue metallic. .	10
Figure 5: Example unit cell of a (4,2) CNT with chiral and translational vectors labeled.	11
Figure 6: (a) Progression of DoS for (2,0), (4,0), and (8,0) CNTs showing progression of vHSs. (b) Katura plot showing vHS positions as a function of CNT diameter (red: semiconducting, blue: metallic) . . .	12
Figure 7: Phonon dispersion relation of monolayer graphene.	15
Figure 8: Raman spectrum of a single CNT with D, G, and 2D peaks labeled.	16
Figure 9: (a) Band diagrams of metals and semiconductors and their junctions (b) according to the Schottky-Mott model and (c) with potential Fermi level pinning effects.	19
Figure 10: Basic (a) physical architecture and (b) band structure schemes of a CNT-FET device.	19
Figure 11: Example schematic of hole injection in a Schottky barrier FET under various operating conditions (a) unbiased, off state, (b) biased, off state, (c) biased, threshold state with thermionic emission, (d) biased, post-threshold/on state with thermionic and field emission. Source and drain electrodes are designated by “S” and “D,” respectively.	21
Figure 12: Gate-source characteristics of a single CNT showing majority electron charge transport regimes.	22
Figure 13: Raman G-band spectrum of a single CNT (a) with polarization vector varied from 0-90° relative to the CNT axis and (b) relative intensity when collected with aligned polarization and CRP.	26
Figure 14: Raman D and G peak intensities of a single CNT plotted with respect to (a) polarization angle, compared against a $\cos^2 \theta$ trendline, and (b) to each other showing that the D/G ratio is linear and independent of polarization.	27
Figure 15: (a) SEM image of a CNT-FET with region of interest indicated. Corresponding Raman spectrum maps of the RBM peak intensity using (b) a horizontally and (c) vertically polarized source	28
Figure 16: Gate-source characteristics of (a) semiconducting and (b) metallic CNTs with V_{DS} varied from -1 V to 1 V in 250 mV increments. . .	29

Figure 17: Gate sweeps of a single CNT with V_{DS} varied from -1 V to 1 V in 250 mV increments at approximately (a) 10^{-9} , (b) 10^{-4} , and (c) 10^0 Torr chamber pressure. (d) Single gate sweeps at each pressure setting shown for comparison ($V_{DS} = 1$ V). Dashed lines indicate locations of I_{DS} minima.	31
Figure 18: (a) Intrinsic CNT-electrode junction with relevant quantities labeled. Increases in Schottky barrier height caused by (b) a change in the electrode work function and (c) a change in CNT electron affinity.	32
Figure 19: Optical pathway of the HR800 system with various optical components labeled: filters (F1, F2), mirrors (M1-M5), neutral-density filter wheel (NDF), half-wave plate mount (HWP), and motor control unit (MCU)	35
Figure 20: (a) Exploded diagram of motorized HWP system (photograph visible in Figure 19). (b) Software control interface (live CCD imaging window not shown).	36
Figure 21: Optical pathway of the HR800 system with QWP mount inserted showing the cleanup polarizer, P1, and the calibration polarizer, P2, which is not utilized during measurements.	37
Figure 22: MEPS chamber overview with accessories labeled.	39
Figure 23: Analog partial pressure histogram scan before and immediately after bake-out and photodesorption process with well known gas species labeled.	40
Figure 24: Gas concentration curves as measured by the RGA as O_2 is injected into the system at approximately $t=0.5$ hrs. Mass-charge ratios are indicated in the legend.	41
Figure 25: Averaged reference spectrum of a CNT used for PCA of all Raman maps	44
Figure 26: Overlapping Raman D-band intensity maps, (a) M_1 and (b) M_2 for a single device before any compositing function is applied.	47
Figure 27: Composite Raman maps of D-band intensity merged by (a) direct overlay and (b) by the described map stitching algorithm.	48
Figure 28: Location of thermionic emission regime in a single gate-source curve. (a) Transconductance, as determined by and iterated 20-channel linear fit with the thermionic cut-off indicated and (b) linear fit of the defined regime in the full gate-source curve.	50
Figure 29: Logarithmic plot of drain-source current characteristics at a fixed gate voltage in the thermionic emission regime. Extrapolation of saturation current from the linear regime (on logarithmic scale) is illustrated.	52

Figure 30: (a) Grid of sixteen CNT-FETs and accompanying test/alignment pads. (b) A single CNT-FET channel with contrast-enhanced channel showing bridging CNT (scale bar corresponds with the host image).	54
Figure 31: Raman spectrum maps of a CNT-FET collected with a circularly polarized source showing (a) D and (b) G peak integrated intensities. (c) Corresponding D/G ratio map.	55
Figure 32: Histogram of D/G ratio of an individual CNT channel with (a) broad distribution and (b) narrow distribution of defects.	56
Figure 33: Histogram of (a) average D/G ratio and (b) number of Raman map points for all CNT-FETs included in this study.	57
Figure 34: Comparison of threshold and off-state gate voltages for each CNT-FET at (a) 3.5×10^{-9} , (b) 3.0×10^{-4} , and (c) 1.0×10^0 Torr chamber pressure ($V_{DS} = 250$ mV). (d) Centroid of (a-c). Error bars indicate one standard deviation centered about the average V_{Go} and V_{th} values.	58
Figure 35: (a) Average change in V_{Go} and V_{Gk} with respect to chamber pressure and (b) corresponding changes for the two chamber pressure transitions (3.5×10^{-9} to 3.0×10^{-4} Torr and 3.0×10^{-4} to 1.0×10^0 Torr).	59
Figure 36: Correlative data showing relationship between (a) gate voltage off-state shift and (b) threshold voltage shift as a function of Raman map points for both chamber pressure transitions (3.5×10^{-9} to 3.0×10^{-4} Torr and 3.0×10^{-4} to 1.0×10^0 Torr). (c) Similar data showing the relationship between gate voltage off-state shift and (d) threshold voltage shift as a function of Raman D/G ratio.	60
Figure 37: Correlative data showing relationship between change in effective Schottky barrier and (a) number of Raman map points and (b) Raman D/G ratio for both chamber pressure transitions (3.5×10^{-9} to 3.0×10^{-4} Torr and 3.0×10^{-4} to 1.0×10^0 Torr). Error bars represent one standard deviation.	61
Figure 38: (a) Cross-section of custom feed-through with Teflon ferrule. Photographs of (a) optical fiber feed-through and (b) clamping fiber armature above a specimen.	78
Figure 39: Schematic of (a) Kelvin probe feed-through and (b) control and measurement electronics.	79

List of Abbreviations/Symbols

Abbreviations

A/O	acoustic/optic (phonon mode)
CCD	charge-coupled device
CNT	carbon nanotube
CRP	continuously rotating polarization
CVD	chemical vapor deposition
DoS	density of states
FET	field-effect transistor
FTIR	Fourier-transform infrared
HWP	half-wave plate
i/o	in-plane/out-of-plane (phonon mode)
IR	infrared
L/T	longitudinal/transverse (phonon mode)
MCU	motor control unit
MEPS	micro-environmental probe station
MW	multi-walled
NA	numerical aperture
NDF	neutral density filter
PCA	principal component analysis
PECVD	plasma-enhanced chemical vapor deposition
QWP	quarter-wave plate
RBM	radial breathing mode
RGA	residual gas analyzer
SEM	scanning electron microscopy
SW	single-walled
UV	ultraviolet
UHV	ultra-high vacuum
vHS	van Hove singularity

Symbols

$\vec{a}_1, \vec{a}_2$	unit cell basis vectors (p. 10)
A_G	Richardson constant (p. 21)
$\vec{c}_h$	carbon nanotube chiral vector (p. 10)
D	Raman D peak (p. 15)
d_t	carbon nanotube diameter (p. 10)
E_d	desorption activation energy (p. 69)
E_{laser}	Raman laser excitation energy (p. 24)
E_{nn}	carbon nanotube electronic energy transition (p. 12)
E_q	charge carrier energy (p. 69)
G	Raman G peak (p. 15)
g	transconductance (p. 49)
h	Planck constant (p. 70)
I	intensity (p. 26)
I_{DS}	drain current (p. 18)
I_S	saturation current (p. 51)
J	current density (p. 21)
J_S	saturation current density (p. 21)
k_B	Boltzmann constant (p. 21)
k_{nm}	cross-correlation coefficient (p. 43)
L_D	mean distance between lattice defects (p. 63)
(n_1, n_2)	carbon nanotube chiral indices (p. 10)
n_d	dopant concentration per unit area (p. 69)
n_D	defect density per unit area (p. 63)
N_C	number of pristine carbon sites (p. 64)
N_D	number of atomic defect sites (p. 64)
N_L	number of available adsorption sites (p. 69)
N_{O_2}	number of occupied adsorption sites (p. 69)
N_T	number of potential adsorption sites (p. 69)
N_v	gas molecules per unit volume (p. 65)
P	chamber pressure (p. 51)
q	charge (p. 21)
s	sticking coefficient (p. 69)
$\vec{T}$	carbon nanotube unit cell translation vector (p. 11)
t_{acq}	Raman acquisition time (p. 26)
$\bar{v}$	average gas molecule velocity (p. 65)
V_{DS}	drain source voltage (p. 17)
V_G	gate voltage (p. 17)
V_{th}	threshold voltage (p. 49)
V_{Go}	off-state gate voltage (p. 58)
z	gas molecule collision rate (p. 66)

$\Delta\Phi_{SB}$	change in effective Schottky barrier (p. 51)
θ	polarization angle (p. 26)
π, π^*	bonding and anti-bonding pi-orbitals (p. 15)
σ	standard deviation (p. 44)
ν	pre-exponential frequency factor (p. 69)
ϕ	gas molecule flux (p. 65)
ϕ_m	metal work function (p. 18)
Φ_{SB}	effective Schottky barrier (p. 18)
χ	semiconductor electron affinity (p. 18)
ω_{RBM}	radial breathing mode frequency (p. 24)

1 Introduction

Since the discovery of the carbon nanotube (CNT) [1], it has been a topic of great interest for material scientists and nanodevice engineers alike. Its unique quasi-1D structure and sp^2 bonding results in a number of interesting optoelectronic and mechanical properties. This has led to investigation of their capabilities as transistors, field-emission electron sources, interconnects, manipulators, heatsinks, and high-tensile fibers, as well as in a variety of composite material and sensing platforms [2–8]. To address the broader impact of this study, the subsequent section discusses some of these innovations in electronic CNT-based devices.

1 Applications of carbon nanotubes

One of the more promising and advanced applications for CNTs is in field-emission electron sources [9,10]. Due to the reliability and ease of fabrication of highly-aligned multi-walled CNTs by plasma-enhanced chemical vapor deposition (PECVD), field-emitters are the most mature CNT-based technology. They have been fabricated by a wide-variety of methods and in range of architectures [11–13]. Due to the high aspect-ratios of CNTs, their promise in this application was immediately foreseen. Their robustness, both mechanical and thermal, has been a further benefit to their promise in this field.

The properties which make CNTs advantageous as electron sources also favorable for vertical interconnects in integrated circuits. Several studies have demon-

strated the use of individual and bundled vertically-aligned CNTs as interconnecting circuits [14]. Li et al have also demonstrated the practicality of traditional chemical mechanical planarization, an obligatory polishing method used in multi-layer device fabrication, to produce CNT interconnect layers [15]. However, a standing difficulty with their application in this field lies in the reliable production of low-resistance ohmic contacts. Advancement of our understanding concerning CNT surface interactions, especially with respect to defects, is paramount towards addressing the problems with CNT contacts.

CNTs have also been heavily studied as candidates for next-generation field-effect transistors (FETs) [16]. Due to the sp^2 bonding of the carbon atoms, conduction band electrons have drastically reduced scattering as they traverse a CNT channel. Indeed, the ballistic transport limit of CNTs have been realized and incredibly promising prototype devices have been evaluated [17]. Two principle challenges exist with the CNT-FET commercialization transition: the previously mentioned difficulty in fabricating reliable contacts, and growth of CNTs with controlled chirality (and thereby electrical performance). While this study does not build upon our understanding of the CNT growth process, it does provide a variety of new measurement techniques which can be invaluable for large-scale testing and evaluation of CNT-FETs.

Building upon the FET platform, CNTs have also been studied as sensors. As this study focuses on the electrical impact of ambient gas environments, it is essential to acknowledge their role as a sensor platform (specifically gas sensors).

There have been numerous studies describing the effectiveness of CNTs as gas sensors [18–20]. A notion cited almost universally in this literature is that surface defects play a substantial role in the chemisorption of gas molecules, and thereby electrical sensitivity. While this hypothesis is sensible, it has not undergone sufficient scrutiny. This aspect of CNT surface-science is foundational to their development as a sensor platform and is of primary interest in this study. While this is presented in context of CNT-based gas sensors, these issues carry over towards the emerging and compelling field of CNT-based biosensors, bioprobes, and other composite-based sensors.

1 Current literature: Status and limitations

While there have been substantial developments in CNT-based devices, as discussed, there are numerous fundamental challenges which must be addressed in order to bridge the gap to CNT commercialization. As mentioned in the abstract, we seek to specifically address the impact of lattice defects on adsorption and the effects of these adsorbates upon the electronic states of the CNT.

Concerning the nature of defect quantification in CNTs by Raman spectroscopy, a substantial body of work has been established [21–23]. These studies systematically address a variety of defect-centric questions about CNTs (some of which are discussed in further detail in section Section 3.1). However, very few studies address the need for Raman mapping techniques [24–26]. Comprehensive methods for defect mapping, which have direct and profound implications on CNT-based electronics, are absent

from this field of study. From this applications standpoint, equal emphasis, if not greater, should be placed upon defect mapping. In this study, we not only develop mapping and quantification techniques, but also apply these techniques to assess the functional role of lattice defects in CNTs in the adsorption process.

Similarly, the electronic properties of CNTs have been well explored, and their response to ambient gases documented. What is lacking, however, is an in-depth analysis and correlative study which can affirm or disprove the mechanisms proposed in the literature which give rise to these electronic phenomena. Indeed, much of the CNT gas sensing studies focus solely on efficacy and device performance, rather than assessing root causes for transport characteristics caused by ambient gases.

1 Approach & organization

This study employs a two-pronged approach to characterize the defect-dependent adsorption and gas sensing of CNT-FETs. The two main experimental thrusts are Raman spectroscopy (an intrinsic material evaluation) and electronic characterizations (which assess device performance) as shown in Figure 1. Using Raman spectroscopy, the polarization-dependent nature of CNTs will be explored and CNT channels will be mapped and analyzed to quantify the number of lattice defects. The electronic characterizations will include gate-source device characteristics with varied ambient pressures. This will allow extraction of critical device parameters which can be correlated against the defect quantification data. In combining these two data, it will be

possible to determine the role of defects in adsorption and to develop models for the CNT-adsorbate interactions.

Figure 1: Flow diagram of experimental approach and techniques applied.

To develop a foundational understanding of the materials presented herein, it is essential to first consider the physical and electronic structure of CNTs. These concepts provide the basis for all observations and must be carefully considered in order to interpret results. While the conceptual links between physical structure and lattice defects (as investigated by Raman spectroscopy) or electronic structure and electronic characteristics may be most evident, there are other important phenomena to consider. Raman scattering events, for instance, also depend upon the electronic structure of the CNT and polarization-dependent effects can not be explained by the physical structure alone.

Following this discussion of fundamental material properties, concepts relevant to the experimentally observed phenomena are introduced. The Raman peaks of interest and corresponding mechanisms are enumerated and basic quantification methodologies are covered. In addition, CNT-FET device architecture is conceptually introduced in terms of the electronic band structure and metal-semiconductor junctions and the corresponding implications for charge transport mechanisms. As this device will be the platform for studying CNTs, these points will be critical in interpreting data and forming meaningful correlations.

In the following sections, these basic physical principals will be cultivated into experimental methods which will guide the study as a whole. Requirements and challenges of Raman spectroscopy of CNTs and a basis for defect quantification and mapping will be covered. Similarly, the general gate-source trends in response to adsorbates will be illustrated and the hypothesized mechanisms for this response will be outlined. As the objectives of this study mandate new measurement techniques, the instrumentation developments carried out over the course of these experiments are also discussed.

Once the nature and mechanism of the measurements are discussed, it is possible to outline the computational methods employed which will translate these measurements into quantities of interest. Since this study focuses on forming larger scale correlations between numerous measurements, the computational works are relatively extensive. In the Results and Discussion sections, a summary of the statistics and

correlations will be presented.

In the concluding remarks of this work, the important results will be discussed and summarized in relation to the hypothesized mechanisms for the adsorbate-CNT interactions. In addition, limitations, challenges, and opportunities for expanding these works will be explored.

2 Experimental Concepts

2 Physical and electronic structure of carbon nanotubes

Bearing the previously presented dilemmas of CNT-FET operation in mind, we must have a complete understanding of CNT structure (physical and electronic). Only then is it possible to design an experiment to test these electronic phenomena and provide meaningful interpretations. Since CNTs are readily visualized as a rolled graphene sheet, graphene is the natural starting point for a discussion of structure. Indeed, throughout this study, graphene will continue to be the basis for the most foundational knowledge of CNTs. Graphene is a 2D sheet consisting of a hexagonally-arranged sheet of sp^2 bonded carbon atoms [27–29]. The corresponding unit cell and first Brillouin zone is depicted in Figure 2.

Figure 2: (a) Unit cell and (b) first Brillouin zone of monolayer graphene

When discussing structure, it is also important to develop an understanding of crystalline defects (as previously mentioned, this study will focus on the nature of these defects). There are several principal lattice formations which will contribute

towards future discussions of defects. These include: (1) single-atom vacancies (monovacancies), (2) two-atom vacancies (divacancies), (3) Stone-Wales defects (in which a single bonded pair of carbon atoms is rotated 90°), and (4) sp^3 coordinated carbon atoms (out-of-plane amorphous clusters) [30–32]. The first three lattice defects are represented in Figure 3. The principle impact of these defects is in Raman spectroscopy and will therefore be discussed in greater detail in later sections.

Figure 3: (a) Pristine graphitic carbon and (b) monovacancy, (c) divacancy, and (d) Stone-Wales defects

As previously stated, the structure of CNTs can be readily visualized as a rolled graphene sheet. The complete description of the CNT thereby requires specification of the structural boundaries of the rolled sheet [33–35]. Two basis vectors, $\vec{a}_1$ and $\vec{a}_2$, are defined in the graphene plane and are equivalent by transformation to the unit cell basis. The principal difference being that they connect atomic sites within the unit cell.

Since the boundary conditions of the rolled sheet require that equivalent lattice points are connected, the graphene sheet can be expressed as integer multiples of the two basis vectors (Figure 4). And further, due to the mirror symmetry between the

Figure 4: Schematic of 2D basis for CNTs with chirality boundary points labeled. Red indicates semiconducting chiralities, and blue metallic.

two vectors, all possible CNTs can be described by the set of boundary conditions enclosed in a 30° angle between the two basis vectors. The chiral vector, $\vec{c}_h$, is thereby defined as

$$\vec{c}_h = n_1 \vec{a}_1 + n_2 \vec{a}_2 \quad (1)$$

With the chirality of a CNT most commonly expressed using (n_1, n_2) notation. Since the chiral vector also defines the circumference of the CNT, the diameter can be trivially expressed as follows:

$$d_t = c_h / \pi \quad (2)$$

A unit cell translational vector, $\vec{T}$, is also defined (perpendicular to $\vec{c}_h$) which

is parallel to the CNT axis

$$\vec{T} = [(2n_2 + n_1)\vec{a}_1 - (2n_1 + n_2)\vec{a}_2] / d_R$$

$$d_R = \begin{cases} d & \text{if } (n_1 - n_2) \text{ is not a multiple of } 3d \\ 3d & \text{if } (n_1 - n_2) \text{ is a multiple of } 3d \end{cases} \quad (3)$$

where d is the greatest common factor of (n_1, n_2) . This final condition is required to assure that the plane perpendicular to the terminus of $\vec{T}$ is equivalent to that at its beginning. Figure 5 provides a schematic illustration of a (4,2) CNT as an example.

Figure 5: Example unit cell of a (4,2) CNT with chiral and translational vectors labeled.

While the overall structure of the CNT is composed of a wrapped graphene sheet, the boundary conditions that describe the diameter have profound implications with respect to the electronic structure. Due to this periodic boundary condition, 1D

Figure 6: (a) Progression of DoS for (2,0), (4,0), and (8,0) CNTs showing progression of vHSs. (b) Katura plot showing vHS positions as a function of CNT diameter (red: semiconducting, blue: metallic)

energy bands form and correspondingly, van Hove singularities (vHS) in the density of states (DoS) are observed [35]. The nature of these singularities and their relationship to the diameter of the CNT can be further understood by comparing an (n_1, n_2) chirality to an (mn_1, mn_2) chirality (where m is an integer). That is, a CNTs with an equivalent chiral angle and a diameter which is an integer multiple greater. This is illustrated in Figure 6a.

Note that as the diameter is successively doubled (from (2,0), to (4,0), to (8,0) chirality), so are the number of vHSs in the given energy range. The energy transitions between vHSs are notated as E_{nn} where n is an integer which indexes the vHS position relative to the Fermi level (e.g. the transition from the first band below the Fermi level to the first band above is noted as the E_{11} transition). Further note that each chirality retains the singularities of its chiral factors by necessity of

the periodic boundary conditions. These singular points can be summarized for all chiralities in so-called “Kataura plots” (Figure 6b) [34]. In addition, there exists a chirality condition for which the density of states is non-zero and continuous near the Fermi energy [33]. Such CNTs are considered metallic in character, lacking the well-defined gap of states between the first vHS above and below the Fermi level observed in semiconducting CNTs. In truth, the electronic characteristics of such CNTs may be referred to as “semimetallic” as they retain drain current saturation and gate-dependence but simply lack a biased “off” state (that is, they are zero band gap semiconductors). The chirality condition for metallic CNTs is as follows (where m is an integer):

$$2n_1 + n_2 = 3m \tag{4}$$

Much like single/multilayer graphene, CNTs can grow either single-walled (SW) or multiwalled (MW), depending upon growth conditions. While SW-CNTs can be either semiconducting or metallic in character, MW-CNTs are almost always metallic as their electronic properties are a superposition of the concentric tubes (i.e. with more chiralities contributing towards the overall electronic properties comes a greater chance of any single chirality satisfying the metallic condition). These electronic properties will be central towards our understanding of device performance in CNTs and second-order Raman scattering events.

2 Raman scattering in graphitic compounds

Raman spectroscopy is a technique which can be used to probe the solid state properties of materials. Primarily, this involves the measurement of the frequencies of lattice vibrations (phonons) which are characteristic of specific crystalline structure. This is performed by incident photons either scattering off of phonons or creating phonons and measuring the relative frequency shift (Raman shift) of these photons as they are re-emitted from the sample. In this way, the frequency shift of a Raman peak directly corresponds to the frequency of the phonon generated. The intensity of these peaks are highly dependent upon the polarizability of bonds (and thereby the polarization of incident photons) as opposed to Fourier-transform infrared spectroscopy (FTIR), a similar technique which largely studies polar oscillations and is most widely used for identifying functional groups of materials. These two techniques are thereby complimentary and widely used in materials science and chemistry.

Once again, to understand these phenomena in CNTs, graphene must be first considered. Figure 7 shows the phonon dispersion relation for graphene, indicating the important phonon modes. Modes are annotated with the following abbreviations: i, in-plane; o, out-of-plane; L, longitudinal; T, transverse; A, acoustic; and O, optic (e.g. iLO and oTA refer to the in-plan longitudinal optic and out-of-plane transverse acoustic modes, respectively). While only monolayer graphene is presented, there is little functional variation when additional layers are introduced. Based upon the plane-polarization of the incident radiation, only the 2D Brillouin zone needs to be

considered [36–38].

Figure 7: Phonon dispersion relation of monolayer graphene.

There are two peaks of interest which are visible in both graphene and CNTs: the G and D peaks. The mechanisms behind these peaks are as follows:

- G: This is a first-order Raman event which involves the scattering of an incident photon off of the degenerate iTO and iLO phonon modes at the Brillouin zone center (Γ point). This phonon is characteristic of graphitic carbon compounds and is present in both graphene and CNTs [39].
- D: The D peak is a second order Raman event which arises due to an incident photon first exciting a valence electron into the conduction band ($\pi \rightarrow \pi^*$ electronic transition). The electron then undergoes inelastic scattering off of an iTO phonon near the K-point, followed by an elastic scattering event off of a defect. A photon is then emitted due to electron-hole recombination. The Raman shift of this photon is equal to the phonon energy of the iTO phonon [30, 37, 40–42]. Since this Raman shift is dependent upon the electron-

phonon-coupling of an electron first being excited into the conduction band, this Raman shift is dependent upon excitation energy. Higher energy photons will result in electronic transitions further from the K-point, and therefore result in scattering off of higher frequency iTO phonons, as per the phonon dispersion relation (Figure 7) [43].

These two peaks can be observed in the example Raman spectrum presented in Figure 8. Note that there is a third peak labeled in this spectrum, the 2D peak (also referred to as the G' peak in rare circumstances). Much like the D peak, the 2D occurs due to a double-resonance process with the exception that the 2D peak does not involve defect scattering, but rather double-scattering with an iTO mode phonon. In graphene, this peak can be used to quantify the number of graphitic carbon layers but the 2D peak plays no role in the present study.

Figure 8: Raman spectrum of a single CNT with D, G, and 2D peaks labeled.

In addition, CNTs can produce a peak which is characteristic of their chirality, called the radial breathing mode (RBM). This peak has some special qualities which arise as a result of the quasi-1D structure of CNTs. As the name suggests, this

peak results from a oTA phonon mode in which the displacement is radially outward, perpendicular to the CNT axis [44,45]. The boundary conditions of this mode cause its frequency to be dependent upon upon the diameter (and thereby the chirality) of the CNT. In addition, the Raman scattering cross-section for the RBM peak is greatly enhanced when an E_{nn} electronic band transition occurs. In fact, in order for the RBM peak to be of measurable intensity, the excitation source of the Raman spectrometer must coincide within 100 meV of an E_{nn} band transition in the CNT under investigation [35,44]. This condition is termed “resonant Raman spectroscopy.”

2 Carbon nanotube field-effect transistors

In addition to the basic band theory of CNTs, as discussed in Section 2.1, the nature and phenomena observed at metal-semiconductor junctions must be considered in order to have a comprehensive understanding of the CNT-FET operation. The basic design of a CNT-FET is not unlike a typical silicon-based FET and the same fundamental principles govern charge carrier transport. Two metal electrodes (source and drain) are connected by a semiconducting channel (the CNT). A gate electrode spans the channel, insulated from the previous three components, typically by an SiO_2 layer. The drain-source bias, V_{DS} , provides a potential difference to move charge carriers across the semiconducting channel. The gate voltage, V_G , applies an electric field to the channel, distorting its electronic bands, allowing charge carriers to transfer between either electrode and the channel.

If a metal and semiconductor are brought into contact in this way, reaching thermodynamic equilibrium, the Fermi level of the two materials will match and a Schottky barrier, Φ_{SB} , will form between the free conduction electrons of the metal and the conduction band of the semiconductor. This barrier is the result of a mismatch between the metal-vacuum work function, ϕ_m , and the semiconductor-vacuum electron affinity, χ , according to the following relation:

$$\Phi_{SB} = \phi_m - \chi \quad (5)$$

Figure 9 schematically illustrates the Schottky barrier phenomenon for arbitrary metal-semiconductor junctions. The barrier height can be modulated by variation in the work function, or by doping of the semiconductor. Junctions with incredibly small barriers are termed “Ohmic contacts” due to their linear drain-source current (I_{DS}) characteristics. Under this model, known as the Schottky-Mott model [46,47], the electrode work function and semiconductor electron affinity determine a great deal about the device characteristics.

The Schottky-Mott model of metal-semiconductor junctions is, however, somewhat naive. Since the electron wave function must be continuous across the junction, there is a finite penetration of states from the metal into the semiconductor surface (often referred to as metal-induced gap states, due to their residence in the semiconductor band gap). Similarly, surface defects in the semiconductor at the interface can act as electron traps, increasing the electron concentration. These effects can cause

Figure 9: (a) Band diagrams of metals and semiconductors and their junctions (b) according to the Schottky-Mott model and (c) with potential Fermi level pinning effects.

the Fermi level to be deviate from the position which would otherwise be expected by the Schottky-Mott rule (as illustrated by example in Figure 9c). In many cases this can cause the Fermi level to be pulled toward the band gap center regardless as to the difference in work function, an effect known as “Fermi level pinning.”

Figure 10: Basic (a) physical architecture and (b) band structure schemes of a CNT-FET device.

A complete CNT-FET device can be fabricated by forming conduction channel interfaces with source and drain electrodes alongside an insulator-isolated gate electrode (Figure 10a) which can be used to distort the CNT channel bands (Figure 10b), permitting the transfer of charge carriers across the source and drain interfaces. This type of device is known as a Schottky barrier FET, modeled as two back-to-back Schottky diodes.

2 Charge carrier transport

Having established the fundamental principles of metal-semiconductor junctions, the mechanisms of charge transport across these junctions can be explored. While FETs are often categorically stated as being in “on” or “off” states, it is necessary to consider a range of operating conditions which showcase the different transport mechanisms. Without a drain-source bias (V_{DS}), and thereby no applied field, charge carriers will not cross the source and drain junctions (Figure 11a). Though, even for non-zero V_{DS} (Figure 11b), charge carriers may not be sufficiently energetic to traverse the energy barrier at the metal-semiconductor junction (whether it be the barrier from the metal Fermi level to the semiconductor valence band for holes, or the semiconductor conduction band for electrons). Note that FETs with a metallic CNT channel will always exhibit some drain-source current (I_{DS}) when biased due to their band of energy states at the Fermi level.

Once a sufficient gate voltage, V_G , is applied, the resulting electric field perturbs the energy bands of the CNT channel and reduces the effective potential barrier allowing charge carriers to transit the junction. In the earliest stages of transport, energetic charge carriers simply transit over the Schottky barrier, a process known as thermionic emission. As presented in Figure 11c, excited holes overcome the energy barrier at the source electrode junction, and are accepted into valence band states of the CNT. The thermionic emission obeys an exponential relationship relative to the applied bias wherein the current density, J , is governed by the following model

Figure 11: Example schematic of hole injection in a Schottky barrier FET under various operating conditions (a) unbiased, off state, (b) biased, off state, (c) biased, threshold state with thermionic emission, (d) biased, post-threshold/on state with thermionic and field emission. Source and drain electrodes are designated by “S” and “D,” respectively.

(where A_G and k_B are the Richardson and Boltzmann constants, respectively):

$$J = J_S \left(e^{\frac{qV_{DS}}{k_B T}} - 1 \right) \quad (6)$$

$$J_S = A_G T^2 e^{\frac{-q\Phi_{SB}}{k_B T}} \quad (7)$$

As the gate field is further increased, the energy bands of the channel further distort, reducing the physical depth of the Schottky barrier, allowing quantum mechanical tunneling of these charge carriers through the barrier (in addition to any thermionic emission), as illustrated in Figure 11d. This phenomenon, known as field emission, becomes the dominant transport model once the magnitude of V_G is sufficient to cause the semiconductor band occupied by the charge carriers (conduction

and valence for electrons and holes, respectively) to cross the Fermi level of the donating electrode. As previously mentioned, the thermionic and field emission transport mechanisms can occur simultaneously in the channel and numerical analysis utilizing these models can be simplified by assessing a regime in which a single mechanism dominates charge transport. These regimes are illustrated approximately in Figure 12.

Figure 12: Gate-source characteristics of a single CNT showing majority electron charge transport regimes.

3 Experimental Methods

3 Quantitative Raman spectroscopy

A variety of methods can be employed to derive quantitative information from Raman spectra of CNTs and graphene. The analysis most pertinent to this study involves the quantification of defects. Since the Raman D peak involves scattering off of a defect, we can weight the intensity of the D peak relative to the intensity of the G peak (a reference intensity which is not dependent upon an electronic transition) in order to quantify the relative number of defects in the graphitic carbon lattice [43, 48]. In the case of graphene, lattice boundaries with dangling p_{xy} orbitals constitute defects, thereby necessitating additional controls for flake size. This effect does not play a significant role in defect quantification for CNTs, however.

In the existing literature, the D/G ratio has been paired with scanning tunneling microscopy to compute an empirical relationship between the D/G ratio and absolute defect densities [31, 49, 50]. In these studies, graphene samples were also subjected to ion bombardment to introduce controlled numbers of defects, producing a gradient of defect densities. This allowed for defect density regimes to be more rigorously defined and allowed for more accurate use of the D/G ratio as a comparative measurement. This type of measurement will be of primary interest for this study.

The primary points of interest in this study are that: (1) the absolute number of defects can be quantified directly from the D/G ratio, (2) the relationship between

defect density and D/G ratio is non-linear and, for sufficiently large ratios, becomes non-monotonic, (3) the wavelength of the excitation source must be taken into account (which was, up until that point, expected as a matter of course), and (4) that other spectral features (which include peak width) may be helpful in identifying regimes of defect density. While prior studies have used the D/G ratio as a quantification metric, this was the first comprehensive effort to express the D/G ratio progression and validates its current use. These absolute quantification models will be applied and discussed in Section 7.1.

In addition to defect quantification, Raman spectroscopy can be used to determine the chirality of an individual CNT if an RBM peak is observed. To do so, one must first note the E_{nn} transitions that correspond with the excitation source energy (E_{laser}). Then, the diameter of the CNT can be calculated from the RBM peak frequency using the following formula [51]:

$$d_t = 248/\omega_{RBM} \quad (8)$$

where d_t is in nm and ω_{RBM} is in cm^{-1} . Note that the constant, 248 $\text{cm}\cdot\text{nm}$, is determined empirically and encompasses a variety of more fundamental physical properties (there are other variations of this relationship with additional correction factors). Combining the values for E_{laser} and d_t , a single point can be located on the Katura plot (Figure 6b) which corresponds to the E_{nn} , d_t combination of a specific chirality.

While the chirality of a CNT is the determining factor in its optoelectronic

properties, the RBM peak is not used for chirality identification in this study. As mentioned, the RBM frequency is dependent upon excitation energy. As the excitation source must be within approximately 100 meV of the vHS separations in the DoS, Raman spectrometers with fixed-wavelength excitation sources are inherently handicapped in their ability to produce and detect RBM phonon scattering.

3 Polarization-dependent Raman spectroscopy

In addition to the previously discussed implication of the quasi-1D structure of CNTs, Raman intensity is strongly correlated with the polarization of the excitation photons with respect to the CNT axis [24, 25]. In order to evaluate this effect, Raman spectra were collected using a 532 nm excitation source from single CNTs (further spectrometer details can be found in Section 4.1).

A half-wave plate was used to rotate the polarization of the beam one complete revolution, collecting spectra at 10° polarization intervals. Figure 13a depicts the variation in G peak intensity for a single CNT subjected to these incident polarizations. An alternative method to incrementally rotating polarization is continuously rotating polarization (CRP) of the excitation source. By rotating the wave plate through an integer multiple of quarter revolutions during the acquisition time (that is, an integer number of 180° changes in polarization), it is possible to collect an averaged spectrum which removes polarization-dependent effects from the observed spectrum. The convenience of this result comes at the expense of measured intensity

relative to measurements with the incident polarization parallel to the CNT axis, as shown in Figure 13b.

Figure 13: Raman G-band spectrum of a single CNT (a) with polarization vector varied from 0-90° relative to the CNT axis and (b) relative intensity when collected with aligned polarization and CRP.

The reduction of intensity due to CRP by approximately 1/2 as observed in Figure 13b is as expected. Since the Raman scattering event requires incident polarization parallel to the CNT axis, the number of Raman scattering events will be proportional to the cosine of the angle, θ , between them. The measured intensity (i.e. the magnitude of the Poynting vector), which is proportional to the square of the electric field, will thereby follow a $\cos^2 \theta$ relationship. If the polarization is rotated continuously for an integer number of revolutions through spectrum acquisition, the time-averaged intensity, $\bar{I}$, is given by:

$$\bar{I} = \frac{1}{t_{acq}} \int_0^{t_{acq}} I_0 \cos^2 \left(\frac{m\pi t}{t_{acq}} \right) dt = \frac{I_0}{2} \quad (9)$$

Where t_{acq} is the acquisition time, I_0 is the maximum observable intensity (wherein the polarization vector is parallel to the CNT axis, or $\theta = 0$), and m is an inte-

ger. This relationship is further validated by plotting the intensity of the D and G peaks (Figure 14a) with respect to θ , which shows a strong correlation with a $\cos^2 \theta$ relationship.

Figure 14: Raman D and G peak intensities of a single CNT plotted with respect to (a) polarization angle, compared against a $\cos^2 \theta$ trendline, and (b) to each other showing that the D/G ratio is linear and independent of polarization.

Plotting the measured D peak intensity against θ further validates the $\cos^2 \theta$ relationship (Figure 14a). Noting this, the D and G intensities scale linearly with one another, as shown in Figure 14b. That is, the D/G ratio is independent of incident polarization and can be effectively computed so long as the polarization conditions yield sufficient spectrum intensity. This in turn validates the use of the D/G ratio as a quantification metric with CRP Raman spectrum acquisition. While these conclusions may seem ancillary in the context of single point spectra (especially where use of a half-wave plate is feasible to manipulate the incident polarization), they are of central importance for Raman mapping, and defect quantification, of CNT-FETs.

Such methods to remove polarization-dependence must be developed for the sake of spatially mapping spectrum variations in CNTs. Growth of CNTs will, in the

Figure 15: (a) SEM image of a CNT-FET with region of interest indicated. Corresponding Raman spectrum maps of the RBM peak intensity using (b) a horizontally and (c) vertically polarized source

absence of extensive external controls, occur following a completely arbitrary path. If a fixed polarization is used to acquire a spectrum map, the intensity of various peaks will be more indicative of the relative polarization than actual scattering effects in the material. This effect is illustrated in Figure 15, wherein the RBM intensity of a single, highly contoured, CNT was mapped. The CRP spectrum technique is therefore of great interest, especially with regards to defect mapping. After all, mapping with fixed polarization would require the acquisition of a redundant map to acquire signal from regions where the CNT path was perpendicular to the original polarization, consuming many additional hours of laser lifetime. In addition, great care and consideration would be required when correlating these maps. Beyond stitching errors in locations where the CNT axis drastically changes direction, the impact of variations in signal-to-noise ratio within individual maps must be mitigated.

3 Electron transport measurements

Measurement of the basic gate- and drain-source characteristics of the CNT-FETs can provide a wealth of knowledge about intrinsic properties of the CNT channel. Most notably, from the gate-source characteristics of the FET, it can be directly observed whether the CNT is metallic or semiconducting as shown in Figure 16. Since metallic CNTs have a constant non-zero DoS near the Fermi level (chiralities specified by the condition in Equation 4), a drain-source bias will always allow current to cross the channel regardless of the gate voltage. Some gating characteristics are still observed due to the vHSs and the relatively low DoS in the mid-gap region (which contribute towards the metallic behavior). This is in contrast with the purely semiconducting CNTs which have no metallic characteristics and thereby have higher on/off ratios. From these overt differences it is possible to discern whether the CNT falls into the metallic or semiconducting subset of chiralities.

Figure 16: Gate-source characteristics of (a) semiconducting and (b) metallic CNTs with V_{DS} varied from -1 V to 1 V in 250 mV increments.

3 Electrical impact of adsorbates

Previously, it was introduced that the electron transport properties of CNT-FETs are dependent upon the composition of the ambient atmosphere. One would indeed hypothesize this to be the case for a transport channel which is composed entirely of surface atoms. In order to measure the intrinsic properties of the CNT-FET (that is, absent surface-adsorbed gas molecules which impact the device characteristics), a probe station must include a chamber pumped down to ultra-high vacuum (UHV) conditions. In the process, the sample and chamber surface are subject to a desorption process (usually a bake-out) to drive off the weakly-adsorbed surface molecules. Note that bake-out temperatures are far lower than what would be required to cause morphological changes to the CNT-FETs. After the temperature has stabilized and the chamber pressure is sufficiently low, the intrinsic characteristics can then be measured. To measure the response of a particular gas species, controlled quantities of the gas must be introduced into the chamber in order to reach a desired working pressure for additional measurements. Such a comparison is presented in Figure 17, wherein the gate-source characteristics of a single CNT-FET were measured under various pressure conditions (as indicated in the figure).

Immediately visible in these data is the shift in the CNT-FET “off” state (and thereby the threshold gate voltages). Two principal mechanisms have been offered in the current literature to account for this threshold voltage shift, revolving around modulation of the Schottky barrier formed at the metal-CNT interface and doping of

Figure 17: Gate sweeps of a single CNT with V_{DS} varied from -1 V to 1 V in 250 mV increments at approximately (a) 10^{-9} , (b) 10^{-4} , and (c) 10^0 Torr chamber pressure. (d) Single gate sweeps at each pressure setting shown for comparison ($V_{DS} = 1$ V). Dashed lines indicate locations of I_{DS} minima.

the CNT channel.

The first mechanism suggests that the shift in threshold voltage is due to a change in contact potential (and thereby, the work function) of the electrode materials due to the adsorption of gases to the surface. While it is well known that the work function of metals can be modulated by annealing in a forming gas (indeed, this is a well utilized procedure in semiconductor manufacturing facilities to assist with barrier tuning), work functions have also been shown to change in the presence of various gas species [52]. Since it is possible for CNTs to have very narrow band gaps (many on the order of 0.25 eV), even slight changes in work function could result in a large

impact on the threshold voltage.

An example of this mechanism is depicted schematically in Figure 18b, where an increase in work function results in an increased Schottky barrier for electrons at the CNT-electrode junction (and a corresponding decrease in the barrier for hole injection). Recalling the charge transport mechanisms discussed in Section 2.4 (specifically as represented in Figure 11), it is clear that these effects will impact the amount of drain current measured with a given gate and drain bias, manifesting as a threshold voltage shift.

Figure 18: (a) Intrinsic CNT-electrode junction with relevant quantities labeled. Increases in Schottky barrier height caused by (b) a change in the electrode work function and (c) a change in CNT electron affinity.

The principal mechanism reported in the literature offers that the ambient O_2 molecules attach to defect sites on the surface of the CNT, acting as p-type dopants or traps for negative charge carriers. These charge traps result in a downward shift of the Fermi level in the CNT due to decreased electron occupancy, which in turn modulates the Schottky barrier of the junction, as illustrated in Figure 18c [53–57].

While both of these mechanisms fundamentally revolve around the Schottky barrier height, the second mechanism, which is more widely accepted, has some additional caveats which make it particularly ripe for consideration in the present study. Much of the present literature postulates that greater concentrations of CNT surface defects will result in increased surface adsorption of ambient gases which should, in turn, increase the magnitude of threshold voltage shifts observed in the gate-source curves at varied oxygen concentrations [57–59].

By applying the previously described quantitative Raman methods in conjunction with the gate-source characteristics, it will be possible to provide a correlation between defect concentrations in the CNT channel to the threshold voltage shifts, and thereby validate the adsorbate doping model for CNT gas sensing.

4 Instrumentation Developments

In order to discern whether or not CNT lattice defects play a role in adsorption of ambient oxygen, and thereby influence threshold voltage in the CNT-FET device, there are two principal requirements of measurement and testing instrumentation: (1) a Raman spectrometer with a high-resolution stage capable of spatial mapping and manipulation of incident beam polarization, and (2) a probe station which can perform the necessary 3-probe measurements while also controlling and characterizing trace-level ambient gases. These requirements initiated several instrumentation developments for polarization control in a commercial Raman spectrometer and the construction of a custom ultra-high vacuum probe station system.

4 Raman spectrometer

Raman spectra for this study were collected using a Horiba LabRAM HR800 Raman/photoluminescence spectrometer. This system is equipped with a 532 nm, 100 mW diode-pumped solid state laser, and a 325 nm, 15 mW HeCd gas laser. Of the objective lenses available on the instrument, a 50x 0.55 NA lens was used for mapping and characterization. For mapping functionality, two stages are attached: a large-range motorized stage and a piezoelectric XY-scan stage capable of 50 nm step intervals over a range of $\pm 200 \mu\text{m}$ relative to the equilibrium position. The optical pathway of the system is depicted in Figure 19. The clean-up filters at the entrance have a 2 nm spectral width, and the dichroic cut-off filters at the objective-end have

reflection/transmission edges steeper than 100 cm^{-1} .

Figure 19: Optical pathway of the HR800 system with various optical components labeled: filters (F1, F2), mirrors (M1-M5), neutral-density filter wheel (NDF), half-wave plate mount (HWP), and motor control unit (MCU)

4.1.1 Motorized half-wave plate

The motorized half-wave plate (HWP) system consists of a 532 nm half-wave plate inserted into a custom mounting block which is engaged by a stepper motor via a pair of miter gears. Rotation of the HWP was stabilized with a roller bearing sleeve (Figure 20a). The stepper motor allows the HWP to be rotated in minimum steps of 1.8° , which corresponds to a 3.6° step in polarization angle. If desired, this could be reduced further by introducing mechanical advantage in the miter gears. A custom software application (Figure 20b) was written to control the HWP during spectrum acquisition. This application mimics all operations of the manufacturer-

supplied control software: neutral density filter (NDF) selection, CCD camera image acquisition, spectrum collection parameter control (acquisition time, accumulations, grating selection, etc), and stage control for mapping functionality. The software adds the HWP control, allowing two principle modes of acquisition: (1) the previously mentioned CRP technique, and (2) incremental polarization rotation for polarization-dependent point spectra. In addition to the schematics and screenshots offered in Figure 20, the mounting bracket can be observed top-down in the photograph in Figure 19.

Figure 20: (a) Exploded diagram of motorized HWP system (photograph visible in Figure 19). (b) Software control interface (live CCD imaging window not shown).

4.1.2 Quarter-wave plate optics

In addition to the motorized HWP system, a quick-change mount (used in place of the HWP mount) was fabricated to allow 3 optical components to be slid into and out of the beam path (Figure 21). Using this mount, a quarter-wave plate (QWP) could be inserted and used to circularly polarize the Raman source in order to achieve the

same general effect of the CRP technique, removing polarization-dependence from Raman spectrum maps. The QWP was used in this fashion to collect the maps used for defect quantification.

Figure 21: Optical pathway of the HR800 system with QWP mount inserted showing the cleanup polarizer, P1, and the calibration polarizer, P2, which is not utilized during measurements.

By inserting linear polarizers in the slots preceding and following the QWP, it was possible, using a power meter, to calibrate the angle of the QWP to produce circular polarization. Aligning the clean-up polarizer, P1 with the intensity maximum of the source removes ellipticity, while the calibration polarizer, P2, is positioned to extinguish the beam (with its polarization axis oriented perpendicular to P1). Inserting the QWP between P1 and P2, and orienting it such that the exit beam (after P2) is of maximum intensity assures that the light exiting the QWP is circularly polarized, meaning that the polarization of the incident photons (from P1) are at a 45° angle with respect to the fast/slow axis of the QWP. This can be further validated by rotating P2 through 180° and observing no change in intensity. The calibration polarizer, P2, is then removed before conducting measurements.

Confidence in well maintained polarization through the spectrometer optics is provided by observing the strong $\cos^2 \theta$ relationship in Figure 14 and the expected 50%

intensity reduction when using the CRP technique (Figure 13). These two results, as presented in Section 3.2 would not be observed without a well maintained polarization state.

4 Micro-environmental probe station

In order to measure the unique electronic response of CNTs to various environmental stimuli, the micro-environmental probe station (MEPS) system was designed and constructed. It consists of an ion-pumped vacuum system that is capable of achieving a base pressure of 3×10^{-9} Torr which is attached to a mini-chamber with 8 additional accessory ports. The ports are loaded with the following: three high-voltage coaxial feed-through probe arms (two of which equipped with software-controlled motors), one fiber armature, a variable gas leak valve with up to 1×10^{-10} Torr·L/s flow rate control, a 4-channel SRS residual gas analyzer (RGA) with an 0.1 ppb measurement floor, vacuum gauges, and a heated/cryogenic stage capable of maintaining sample temperatures from 10-500 K. Additional accessories consist of an Agilent B1500A semiconductor parameter analyzer, Keithly high-voltage power supply (2 kV), and a DelMar Trestles Ti:Sapphire tunable infrared (IR) laser (700-950 nm, 0-350 mW). A labeled chamber overview is depicted in Figure 22.

Figure 22: MEPS chamber overview with accessories labeled.

4.2.1 Gas injection and sensing

The principle goal of the MEPS was to enable the measurement the electronic response of CNT-FETs to ambient gases. The first requirement for such a study is to drive-off adsorbates from the surface of the CNT. This includes a bake-out and ultraviolet (UV) photodesorption process: ramping of the vacuum system to at least 5×10^{-6} Torr (by operating rotary and turbomolecular pumps), followed by an 18 hr whole-chamber and sample bake-out at 200 °C. After allowing the chamber to rest at thermal equilibrium for approximately 12 hrs, an UV lamp (15 W at 250 nm) is then use for 1 hr to induce photodesorption. The benefit of the photodesorption process is two-

fold: higher vacuum levels can be achieved, and molecules with higher enthalpies of desorption (such as H_2O) can be removed from surfaces. In addition, if the use of an RGA is required, the RGA filament should be ramped and degassed before the bake-out procedure in order to avoid the introduction of additional contaminants into the chamber. Figure 23 shows the benefit of the bake-out and photodesorption process. In absolute terms, the bake-out procedure can reduce the ultimate pressure by more than an order of magnitude but of primary interest is that the partial pressure of H_2O is reduced by approximately a factor of 2 relative to nitrogen. In addition, O_2 levels are reduced to the noise floor of the instrument.

Figure 23: Analog partial pressure histogram scan before and immediately after bake-out and photodesorption process with well known gas species labeled.

The injection of gas species itself was facilitated by the addition of the RGA and the variable leak valve. The precision valve allows an inlet of gases (in this case, O_2 was studied exclusively) while pressure and gas concentrations are monitored using the vacuum gauges and RGA, respectively. The combination of the bake-out procedure and gas injection system allow environments to be created with $>95\%$

purity of the target gas species at 5×10^{-6} Torr. Figure 24 shows a logarithmic plot of various gas concentrations as a function of time as O_2 is injected into the chamber (with the RGA in 4-channel live monitor mode). After evacuating and purging the inlet lines and opening the leak valve at approximately 0.5 hrs, the O_2 gas concentration increases by a factor of approximately 10^4 . Whereas N_2 increases by less than a factor of 10 and the increase in water vapor is not sustained after 2 hrs.

Figure 24: Gas concentration curves as measured by the RGA as O_2 is injected into the system at approximately $t=0.5$ hrs. Mass-charge ratios are indicated in the legend.

5 Computational Methods

While the analysis of individual Raman spectra or drain current curves are mathematically trivial, the scale of this correlative study presents numerous computational challenges. Consider the number of data points subject to consideration: For the electronic characterizations, gate sweeps are each composed of 801 data points (I_{DS} vs. V_G values) at 9 different V_{DS} settings. These gate sweeps are collected 3 times and averaged for each of 30 devices across 3 different chamber pressures (1,946,430 unique data points). With respect to Raman measurements, each of the 31 analyzed devices contain an average of 2,958 map points, which are composed of 1,024-channel spectra (intensity vs. Raman shift data points) and their associated map coordinates (90,869,760 unique data points).

The principal consideration is that the scale necessitates custom software with a carefully designed data structure that provides a convient system for parsing source data files, looking up specific data points of interest, iteration through a series of data, storage of computed values, and proof-of-concept computations. While these topics are not discussed in further detail, they are noted as an important point of experimental computational sciences.

From a standpoint of computational methods, this section will clarify the procedure used for extracting values of interest from gate sweep curves, identifying regions of interest in Raman maps, map stitching, and D/G ratio computation in a way which is scalable and limits arbitration bias. Analysis routines were written in

the Python scripting language and can be found in A.

5 Raman region identification

In any form of data analysis, isolating a region of interest is of primary importance. In the case of the Raman maps presented in this study, the region of interest (the CNT channel) represents the minority of the acquired data. Indeed, the majority of the CNT-FETs analyzed compose less than 2.5% of the point spectra in a typical $40\text{ }\mu\text{m} \times 25\text{ }\mu\text{m}$ map. It is therefore of great importance to clearly identify CNT spectra in the map and discard all others from further analysis.

To achieve this, a simple principal component analysis (PCA) algorithm was used. Spectra characteristic of the main regions (SiO_2 background, electrode edges, electrode bulk, and CNTs) were manually extracted from several maps and averaged to produce a spectrum dictionary. Cross-correlation coefficients were calculated and tracked for each point spectrum in the map, $I_n(\omega)$, and reference spectrum $I_m(\omega)$ according to the following relation:

$$k_{nm} = \frac{1}{N} \sum_{\omega} \frac{(I_n(\omega) - \bar{I}_n)(I_m(\omega) - \bar{I}_m)}{\sigma_n \sigma_m} \quad (10)$$

Where N is the number of wavenumber values, ω , or spectrum channels (1,024) and σ_n and σ_m are the standard deviations of the map point and reference spectra, respectively:

$$\sigma = \sqrt{\frac{1}{N} \sum_{\omega} (I(\omega) - \bar{I})^2} \quad (11)$$

Note the exceptional cases where $k_{nm} = -1$, $k_{nm} = 0$, $k_{nm} = 1$ indicate anti-correlation (e.g. $I_n(\omega) = -I_m(\omega)$), perfect uncorrelation (e.g. $I_n(\omega)$ or $I_m(\omega)$ is true noise), and perfect correlation ($I_n(\omega) = I_m(\omega)$), respectively. Though this provides a strong method of spectrum categorization for several principal components, it was found that there was no functional improvement upon a k_{nm} cut-off value for categorizing map points as CNTs. For this reason, the PCA algorithm was simplified slightly to only compute coefficients against the characteristic CNT spectrum, $k_{n,CNT}$, and employ a dynamic cutoff of $k_{cut-off} = (1 - e^{-1}) \max(k_{n,CNT})$.

Figure 25: Averaged reference spectrum of a CNT used for PCA of all Raman maps

While the employed method utilizes an *a priori* reference spectrum, it is noted that a representative n -dimensional component space can be algorithmically achieved, albeit at greater computational expense. Briefly, this method is to generate a sum

spectrum for the whole map, and then to locate regions in the map which have the lowest cross-correlation coefficient with the sum spectrum. In this way, the most linearly independent spectrum components are discovered. Given the fact that a single compound was under investigation with spectrum features sufficiently distinct from surrounding media, the spectrum dictionary method was sufficiently rigorous to isolate regions of interest. If, on the other hand, it was necessary to discriminate between CNTs and other sp^2 carbon compounds, a more algorithmic approach to the component discovery could be warranted.

5 Raman map stitching

Due to the arbitrary growth path of CNTs in the chemical vapor deposition (CVD) process, Raman mapping of CNT-FETs necessitates a degree of prospecting. The CNT channel can span the electrodes by the most direct path (across the 7 μm gap between the electrode fingers) or by any number of meandering paths between the catalyst island and the electrode contact pad (some 50 μm away). The acquisition time for Raman spectroscopy is an added complication. Even for modest acquisition parameters (2 second accumulations time, 3 averaged acquisition), a typical map for this study consisting of approximately 8,400 points would consume 14 hrs. Software overhead and stage translation can result in an additional 4 hours for such mapping operations. This also presumes an ideal condition in which the sine bar governing the grating position does not require adjustment. Without a sufficiently low groove

density, actuating the sine bar to acquire the entire spectral region of interest could consume far more time than the data acquisition itself.

With these points in mind, the general procedure of mapping was to acquire an initial speculative map, then to collect any additional maps according to the expected CNT path. In the process of generating overall D/G ratio statistics, it was necessary to align and stitch together the successive maps and remove redundant points. Two behaviors of the commercial software and hardware resulted in added complications for this procedure: (1) Due to the small fixed range of the piezoelectric stage, it is only employed for translations in the mapping process. Shifting the stage, even within the bounds of the piezoelectric stage, employs the motorized stage. Due to gear backlash, the new mapping center is only accurate within a couple of microns. The absolute coordinates of the map origin must therefore be adjusted to compensate for gaps or excessive overlap depending upon the previous motorized stage translations. (2) In the process of Raman mapping, the recorded stage position corresponds with the true piezoelectric deflection rather than the user-specified mapping parameters. This results in a variation within about 10 nm of the user-specified values and thereby a variable mapping interval. This necessitates a special routine for managing the cross-correlation of points in the maps which require a stitching operation. The entire map stitching operation can be outlined by the following procedure:

(1) For maps M_1 and M_2 , collect all points within M_2 which lie in the potential overlap margin of M_1 , defined as M_{21} . (2) Shift coordinates of all points in M_{21}

by $\vec{\delta}_{nm} = n \, dx \, \hat{\mathbf{i}} + m \, dy \, \hat{\mathbf{j}}$ where $n, m = \{-6..6\}$ and $dx, dy = 350 \text{ nm}$. That is, a 13x13 grid in increments of the user-specified mapping interval. (3) For all points in M_{21} at a given $\vec{\delta}_{nm}$, compute the nearest point in M_1 (within a distance of $0.55dx$). (4) Compute cross-correlation coefficients between M_{21} point spectra and their corresponding M_1 pair and determine the average coefficient, k_{nm} for the given $\vec{\delta}_{nm}$. (5) Repeat for all values of n and m and shift M_2 by the $\vec{\delta}_{nm}$ value for which k_{nm} is maximized. (6) Discard all points in the shifted M_2 which overlap M_1 and merge all points into a single map, M_f .

Figure 26: Overlapping Raman D-band intensity maps, (a) M_1 and (b) M_2 for a single device before any compositing function is applied.

From a standpoint of addressing the previously mentioned concerns, step 2 corrects for motor backlash whereas step 3 compensates for variation in piezoelectric

stage read-out. The use of an averaged cross-correlation coefficient prevents biasing towards positions of maximum overlap. Figure 26 presents an example map of two overlapping Raman maps which require a stitching operation. The composite map is presented in Figure 27 before and after application of the stitching algorithm.

Figure 27: Composite Raman maps of D-band intensity merged by (a) direct overlay and (b) by the described map stitching algorithm.

For the example map presented, M_1 (Figure 26a) and M_2 (Figure 26b) consisted of 318 points and 400 points, respectively, while the overlap domain M_{21} consisted of 131 points. The final stitched map, M_f (Figure 27b) consisted of 566 points (i.e. 152 redundant points removed). Without applying the stitching algorithm, approximately 27% of the legitimate map points would be double-weighted in the final

map statistics. Qualitative inspection of the stitched maps in Figure 26 shows that the redundant points were coincident with a regional minimum in the D-band intensity. This highlights the importance of such a stitching procedure. Without applying the stitching algorithm (i.e. tolerating the overlap redundancy), the average D/G ratio for the channel would be substantially reduced.

5 Effective Schottky barrier

As previously discussed in Section 2.4, the effective Schottky barrier, Φ_{SB} , and threshold voltage, V_{th} , will be used as metrics to discern any influence on the electronic transport properties of the CNT channel. As the thermionic emission regime greatly simplifies the relationship between measurable parameters and the Schottky barrier, computational methods must begin with locating this region of interest, followed by data/parameter extraction.

This was carried out by iterating a linear fit over a fixed gate voltage channel width (20 channels or 1 V) along a gate-source curve, extracting the slope parameter from the fit, and isolating the range in which this slope (that is, the transconductance g) drops by no more than 10% of the maximum (where the thermionic transport mechanism is dominant). This is illustrated in Figure 28a.

The linear window of the thermionic emission regime, once located, is fit linearly (Figure 28b) to extract the threshold voltage, V_{th} (simply the x -intercept). To compute the change in effective Schottky barrier using only the information con-

Figure 28: Location of thermionic emission regime in a single gate-source curve. (a) Transconductance, as determined by and iterated 20-channel linear fit with the thermionic cut-off indicated and (b) linear fit of the defined regime in the full gate-source curve.

tained in the gate sweeps, $\Delta\Phi_{SB}$ must be computed for a static value of V_G and V_{DS} . Therefore, the thermionic emission windows must be stored and compared to find overlapping regimes across chamber pressure settings. Once a range of overlap is determined, $\Delta\Phi_{SB}$ can be computed by re-arranging Equation 7 to solve for Φ_{SB} :

$$\Phi_{SB} = -\frac{k_B T}{q} \left[\ln \frac{I_S}{AA_G T^2} \right]$$

Where A is the channel area (substituting $J_S = I_S/A$). The change in Schottky barrier height, $\Delta\Phi_{SB}$, from chamber pressure P to P' can thereby be expressed as:

$$\Delta\Phi_{SB} = \left[-\frac{k_B T}{q} (\ln I_S - \ln AA_G T^2) \right]_{P'} - \left[-\frac{k_B T}{q} (\ln I_S - \ln AA_G T^2) \right]_P$$

Noting that A , A_G , and T do not change, the expression can be greatly simplified:

$$\Delta\Phi_{SB} = \frac{k_B T}{q} \left[\ln \frac{I_S}{I'_S} \right] \quad (12)$$

Where I_S and I'_S are the drain saturation current values at chamber pressures of P and P' , respectively, at a fixed V_G value. This relationship can then be used to compute the change in effective Schottky barrier at a given value of V_G which lies in the overlapping thermionic emission regimes of devices characterized under different chamber pressure conditions (the change in Schottky barrier due to the presence of adsorbates).

In order to compute the saturation current, I_S , Equation 6 can be re-written in the following form [60]:

$$I_{DS} = I_S e^{\frac{qV_{DS}}{nk_B T}} \left(1 - e^{-\frac{qV_{DS}}{k_B T}} \right) \quad (13)$$

Instead of plotting I_{DS} against V_{DS} , the natural logarithm of $I_{DS}/(1-\exp(-qV_{DS}/k_B T))$ is plotted against V_{DS} (Figure 29). Fitting the linear regime of this logarithmic plot

(that is, the exponential region on a linear scale) allows the saturation current to be extracted from the y -intercept of the graph [60]. These values allow $\Delta\Phi_{SB}$ to be computed directly with using Equation 12.

Figure 29: Logarithmic plot of drain-source current characteristics at a fixed gate voltage in the thermionic emission regime. Extrapolation of saturation current from the linear regime (on logarithmic scale) is illustrated.

6 Results

6 Device fabrication

CNT-FETs were fabricated on conductively doped Si substrates with 100 nm of surface oxide. Catalyst islands ($1.0 \text{ \AA Fe}$) were patterned and deposited on the substrate using photolithography and magnetron sputtering. Growth of CNTs was carried out in a CVD reactor with a Joule-heated graphite stage. A base pressure of 8.5×10^{-2} mbar was achieved before ramping the stage temperature to $925 \text{ }^{\circ}\text{C}$ at $800 \text{ }^{\circ}\text{C/min}$. A carbon feedstock gas (C_2H_2) and a reducing species (H_2) were allowed to flow into the chamber at 690 and 23 sccm, respectively (achieving a working pressure of 10 mbar). After 10 minutes, gas flow and heating current to the stage was ceased. Substrates were then allowed to cool to room temperature in vacuum. Electrodes were then lithographically patterned and deposited by sputtering of Au (250 nm). Devices were fabricated in large 10×10 grids of 6 devices (600 devices per die). Representative images of CNT-FETs are depicted in Figure 30. These fabrication procedures produced 66 operating devices (11 % yield). Devices which exhibited unfavorable electrical characteristics (diode, short circuit, or multi-channel) were excluded from this figure. Therefore, this figure does not represent the number of operational channels fabricated, but rather the pool of operational devices usable in this study.

Figure 30: (a) Grid of sixteen CNT-FETs and accompanying test/alignment pads. (b) A single CNT-FET channel with contrast-enhanced channel showing bridging CNT (scale bar corresponds with the host image).

6 Raman spectroscopy

6.2.1 Defect mapping

Raman maps were collected from 31 single-channel CNT-FETs utilizing 4 mW of circularly polarized light through a 50x 0.55 NA objective (approximately 3.66×10^5 W/cm²). While Raman map acquisition was previously illustrated in Figure 27b, Figure 31 shows representative post-computation D, G, and D/G ratio maps. Figure 31c shows that the defect density of this particular CNT exhibits a gradient in defect density. For the purposes of final analysis, these maps are reduced to a single statistic and therefore serve principally as a visual inspection mechanism to verify the output of computational work.

In order to prevent z-drift of the stage during mapping acquisition, the motorized stage was driven up towards the focal point, shifting the sample plane from

Figure 31: Raman spectrum maps of a CNT-FET collected with a circularly polarized source showing (a) D and (b) G peak integrated intensities. (c) Corresponding D/G ratio map.

an underfocused position. Allowing the stage to rest for two hours prior to mapping further assured that no settling of motor backlash would occur during the mapping acquisition process. No loss of spatial resolution was observed along the raster axis (parallel to the CNT channel), as shown in Figure 31, which suggests that any out-of-plane stage drift was negligible.

6.2.2 Defect quantification

The defect maps (Figure 31c), as derived from the Raman D and G spectrum maps, are a useful means for visualizing the spatial distribution and overall variation in defect density. However, they do not present the defect density in a form which can facilitate comparison between CNTs. To satisfy this need, it is necessary to

construct a defect histogram which shows the number of pixels in the map which fall into a specific interval of D/G ratio. Examples of such histograms are presented in Figure 32, with the histogram featured in Figure 32a corresponding to the map presented in Figure 31. While there was some variation observed in defect density distribution and occasional mild asymmetry in distribution (such as in Figure 32b, no devices exhibited extraordinary (bimodal, for example) distributions.

Figure 32: Histogram of D/G ratio of an individual CNT channel with (a) broad distribution and (b) narrow distribution of defects.

Histograms of the D/G ratios and number of Raman map points for the complete pool of devices included in the study can be seen in Figure 33, with 30-50 points being the most prevalent number points to be found in a map (corresponding with a direct growth between the tips of electrode fingers). Note that approximately 75% of CNTs have D/G ratios less than 0.25 and that the population of measured devices has a relatively even distribution within this regime.

Figure 33: Histogram of (a) average D/G ratio and (b) number of Raman map points for all CNT-FETs included in this study.

6 Electron transport

Measurements of CNT-FET drain current were carried out in the MEPS at varied chamber pressures. In order to drive off adsorbates, the chamber and substrate were subjected to a 200 °C bake-out for 18 hrs after pumping down to less than 5×10^{-7} Torr. During the final 2 hrs of the bake-out cycle, a 15 W 250 nm UV lamp was used to illuminate the stage and chamber to assist with the desorption process. Measurements were carried out for each of 30 CNT-FET devices at three different chamber pressures: 3.5×10^{-9} (base pressure), 3.0×10^{-4} , and 1.0×10^0 Torr. In order to elevate the chamber pressure, O₂ gas was leaked into the chamber gradually using the leak valve. Prior to opening the leak valve, the leading gas lines were pumped and purged iteratively by rotary pump in order to reduce the amount of atmospheric air introduced into the chamber. Concentrations of various gases of

interest were monitored using an RGA (Figure 24 depicts conditioning of the chamber from 3.5×10^{-9} to 5×10^{-6} Torr). The chamber atmosphere was found to be $> 95\%$ O_2 under such conditions.

Figure 34: Comparison of threshold and off-state gate voltages for each CNT-FET at (a) 3.5×10^{-9} , (b) 3.0×10^{-4} , and (c) 1.0×10^0 Torr chamber pressure ($V_{DS} = 250$ mV). (d) Centroid of (a-c). Error bars indicate one standard deviation centered about the average V_{Go} and V_{th} values.

At each previously mentioned pressure setting, gate-source sweeps were collected. Gate voltages were varied from -20 to 20 V in 50 mV increments with V_{DS} ranging from -1 V to 1 V in 250 mV increments. Gate voltage off-state (V_{Go}) and threshold voltage values (V_{th}) were computed from the gate sweeps in accordance with Section 5.3. They are presented in correlative form for each pressure setting in Figure 34. Figure 34d conjointly shows the centroids of all three data clusters to

illustrate the progression in V_{Go} and V_{th} with respect to pressure. These data are similarly expressed in Figure 35, showing that V_{th} tends to remain approximately 3.5 V higher than V_{Go} at each pressure setting.

Figure 35: (a) Average change in V_{Go} and V_{th} with respect to chamber pressure and (b) corresponding changes for the two chamber pressure transitions (3.5×10^{-9} to 3.0×10^{-4} Torr and 3.0×10^{-4} to 1.0×10^0 Torr).

6 Correlations

Having presented the general statistics individually observed in Raman spectroscopy and electronic characterization of the CNT-FETs in the MEPS, the two must be correlated. Figure 36 shows correlative plots of the change in off-state and threshold gate voltage (ΔV_{Go} and ΔV_{th}) with respect to computed D/G ratios and number of Raman map points for each device across the two pressure transitions.

No clear correlation is observed between the gate voltage shifts and the number of map points (which translates directly to the length of the CNT), or with the defect density as determined by the D/G ratio. It is however noted that the shorter channels (less than approximately 100 map points) exhibit a larger spread of gate voltage

Figure 36: Correlative data showing relationship between (a) gate voltage off-state shift and (b) threshold voltage shift as a function of Raman map points for both chamber pressure transitions (3.5×10^{-9} to 3.0×10^{-4} Torr and 3.0×10^{-4} to 1.0×10^0 Torr). (c) Similar data showing the relationship between gate voltage off-state shift and (d) threshold voltage shift as a function of Raman D/G ratio.

shifts, as shown in Figure 36a and Figure 36b. Though this observation is of limited statistical significance due to the small population of devices with greater channel lengths.

When the change in effective Schottky barrier, $\Delta\Phi_{SB}$ is computed (in accordance with the methods presented in Section 5.3) and correlated to these two Raman-derived quantities, the lack of correlation is reinforced. A broad spread is

Figure 37: Correlative data showing relationship between change in effective Schottky barrier and (a) number of Raman map points and (b) Raman D/G ratio for both chamber pressure transitions (3.5×10^{-9} to 3.0×10^{-4} Torr and 3.0×10^{-4} to 1.0×10^0 Torr). Error bars represent one standard deviation.

observed in the change in barrier height, independent of the defect density or channel length. Though it can be noted that the error bars about $\Delta\Phi_{SB}$ are relatively small which indicates that the barrier height varies very little within the thermionic emission regime (with average deviations of approximately 16% and 5% for the first and second pressure transitions, respectively).

7 Discussion

As mentioned in Section 6.4, Figure 36 and Figure 37 clearly show a lack of correlation between any of the device characteristics (shifts in V_{th} and V_{Go} , or changes in Φ_{SB}) and the D/G ratio. These data suggest that the defect density of the CNT channel does not play a substantial role in the device performance and gas sensing metrics. Specifically, the defects do not play a dominant role in the adsorption process and the impact of adsorbates on the device characteristics. In addition, the number of map points (indirectly, the length of the CNT channel) similarly plays no role. Even when considered jointly via a defect-to-length ratio, no correlation is observed. It is therefore necessary to assess, in more concrete terms, what role defects are capable of playing in the modulation of the CNT transport properties in the presence of oxygen.

This will be addressed by considering the following: (1) Quantification of the atomic defect density in the CNT channel and comparison to dopant concentrations; (2) Gas-surface collisions and associated statistics; (3) Chemisorption, physisorption, and charge transfer processes. These concepts, reconciled with the presented data, will be used to propose a model for the gas sensitivity observed.

7 Defect density estimation

In the work by Cançado, an empirical formula was determined for computing the absolute defect density of graphene as a function of the Raman D/G ratio [43, 50, 61]. Expressed in two forms, this formula showed that the average distance between

defects, L_D (nm), and defect density, n_D (cm^{-2}), were given by:

$$L_D^2 = (1.8 \pm 0.5 \times 10^{-9}) \lambda^4 \left(\frac{I_D}{I_G} \right)^{-1} \quad (14)$$

$$n_D = (1.8 \pm 0.5 \times 10^{22}) \lambda^{-4} \left(\frac{I_D}{I_G} \right) \quad (15)$$

Where I_D and I_G are the intensities of the Raman D and G peaks, and λ is the Raman excitation wavelength (nm). Note that this relationship does not hold for relatively high defect densities ($L_D \leq 10$ nm) where a decrease in I_D/I_G is observed, though severe broadening of the D, G, and 2D peaks allow this regime to be easily identified. Assuming that these relations hold for CNTs, much like electronic band structure and portions of the phonon dispersion relation (and thereby, Raman phenomena generic to graphitic compounds), the Raman map data can be used to estimate absolute defect densities of the CNT-FETs in the study.

Using the average D/G ratios for each CNT channel, the average distance between defects was found to be 34.2 nm ($\sigma = 17.4$ nm, $n_D = 4.64 \times 10^{10} \text{ cm}^{-2}$). By combining these values with Raman region map data, an absolute defect quantification can be performed.

The CNT channel surface area can be estimated by first converting the number of Raman map points into an approximate length. As observed in Figure 31, the CNT channel has a diameter of 3-4 points (which was typical among the maps), which

coincides with the Raman excitation spot diameter of 1.18 μm and typical spatial resolution of Raman maps. The CNT channel length can be estimated by dividing the number of map points by 3.5 and multiplying by the mapping interval (350 nm). In estimating the surface area of the CNT, absent a chirality measurement, an assumption might also be made concerning the diameter. While such an assumption may seem to impose a cost to the precision in defect quantification, the functional quantity in this case is the atomic surface density of the CNT, which is invariant of diameter.

Having arrived at an estimated CNT length and surface area ($A = \pi dL$), the raw number of atomic defect sites, N_D can be trivially computed. Similarly, knowing the approximate linear atomic density of a 2 nm diameter CNT (58.37 atoms/nm) facilitates computation of the number of carbon atom sites, N_C , in the CNT channel. This allows the fraction of defect sites, N_D/N_C , to be considered in the same way one would the dopant concentration in a bulk semiconductor. While dopant concentrations are often expressed in terms of volume, the atomic ratio provides a more direct analog. On average, the defect fraction was found to be 4.99×10^{-5} (with a minimum of 3.77×10^{-6} and a maximum of 1.79×10^{-4}).

To compare this with commercial bulk semiconductors, silicon has an atomic concentration of approximately 5×10^{22} atoms/cm³ and dopant concentrations can vary between 1×10^{13} and 1×10^{18} atoms/cm³, depending upon the various desired transport properties. That is, in atomic terms, the dopant fraction is between 1×10^{-9}

and 1×10^{-4} , which encompasses the range of defect densities present in the CNTs in this study. It is important to note that this parallel is only important in so far as these surface defects are considered adsorption sites. It is not expected that intrinsic defects in such concentrations would result in substantial change to electrical characteristics.

7 Gas-surface collisions

If the gas sensing properties of the CNT-FETs is to be attributed to interactions between surface defects and gas molecules, the nature of gas-surface interactions must be discussed as well as the nature of the surface defects. To compute the surface collision rate, it is first necessary to determine the average velocity of a gas molecule and the molecular flux upon a surface in a chamber, which are given by [62, 63]:

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}} \quad (16)$$

$$\phi = \bar{v} N_v A / 4 \quad (17)$$

Where m is the mass of the molecule, N_v is the number of molecules per unit volume, and A is the area of the surface of interest. The flux of O_2 molecules incident upon the CNT channel can thereby be estimated in terms of pressure as follows:

$$\phi = \frac{P}{\sqrt{2\pi k_B T m_{O_2}}} \quad (18)$$

Using values of 295 K and 31.9998 amu for the temperature and molecular mass of diatomic oxygen, respectively, the flux was determined to be 94.9, 8.14×10^6 , and $2.71 \times 10^{10} \text{ } \mu\text{m}^{-2}\text{s}^{-1}$ for chamber pressures of 3.5×10^{-9} , 3.0×10^{-4} , and 1.0 Torr, respectively (and $\bar{v}_{O_2} = 441.8 \text{ m/s}$). From ϕ , it is trivial to compute the number of collisions per second, $z = \phi A$, of the CNT channel (where A is the area of the CNT as estimated in Section 7.1). Correspondingly, with the previously computed defect densities, The average collision rate with the aggregate lattice defects in the entire channel can also be computed. These values are summarized in Table 1.

		P (Torr)		
		3.5×10^{-9}	3.0×10^{-4}	1.0×10^0
CNT	$z_{max} \text{ (s}^{-1}\text{)}$	5.72×10^1	4.90×10^6	1.63×10^{10}
	$\bar{z} \text{ (s}^{-1}\text{)}$	1.72×10^1	1.47×10^6	4.90×10^9
	$z_{min} \text{ (s}^{-1}\text{)}$	1.37×10^0	1.18×10^5	3.92×10^8
Defect	$z_{max} \text{ (s}^{-1}\text{)}$	4.82×10^{-3}	4.13×10^2	1.38×10^6
	$\bar{z} \text{ (s}^{-1}\text{)}$	9.46×10^{-4}	8.11×10^1	2.70×10^5
	$z_{min} \text{ (s}^{-1}\text{)}$	1.82×10^{-5}	1.56×10^0	5.20×10^3

Table 1: Collision rates of O_2 molecules at various pressures with entire CNT channel and with defect sites.

7 Chemisorption and physisorption processes

Having established statistics concerning the number of lattice defects in the CNT channel and collisions between this surface and ambient O_2 molecules, it is necessary to discuss the actual interaction between gas molecules and the CNT surface. This will provide the conceptual linkage between the gas-surface collisions and the pressure dependence of the threshold voltage.

The most extreme adsorption case is that of chemisorption, a process involving the formation of new chemical bonds between the CNT channel and adsorbed gas species. An intuitive consideration suggests that such higher binding energy interactions (on the order of several electron volts [62, 63]) are unlikely in this scenario. Indeed, given that kinetic collisions are the sole mechanism available to initialize the binding event, a room temperature gas is not expected to be capable of causing an ionization event. Integrating the Maxwellian energy distribution for O_2 suggests a probability of 6.86×10^{-51} that an O_2 molecule will have kinetic energy greater than or equal to 3 eV under these conditions. First principles computations have yielded binding energies between 3.58 and 5.06 eV for chemisorbed O_2 onto CNTs of various chiralities [64], suggesting that even this probability is a conservative estimate. With the aforementioned literature values, probabilities of sufficient kinetic energy would range between 9.25×10^{-61} and 5.71×10^{-86} . With an estimated 10^{19} gas molecules in the chamber at 1.0 Torr, the probability that a single molecule has sufficient kinetic energy to initialize chemisorption is vanishingly small.

In further studies, it has been shown that surface-adsorbed O_2 exhibits minimal change in characteristic stretch frequencies relative to the gas phase (from 194 to 191 eV as measured by electron energy-loss spectroscopy) [65, 66]. This is in contrast with the expected energy of 140 eV for chemisorbed O_2^- species [67]. This further supports the notion that chemisorption of O_2 presents a negligible fraction of the gas-surface interactions.

By contrast, physisorbed molecules are bound by Van der Waals with binding energies on the order of a fraction of an electron volt. For graphitic carbon, reported binding energies associated with O_2 physisorption ranged from 104 to 120 meV [68, 69]. Physisorption onto single CNTs occurs with a slightly higher binding energy, with reported values ranging from 120 to 192 meV, depending upon chirality and orientation of the adsorbed molecule [54, 56, 69]. In these same studies, it was computed that a charge transfer of approximately $0.1q_e$ occurs at the adsorbate site (electron donation by the CNT) [54, 56, 59], suggesting that adsorbed O_2 molecules can act as p-type dopants. Repeating the same integral of the Maxwellian distribution yields a probability between 2.40×10^{-2} and 1.73×10^{-3} that a given O_2 molecule will have kinetic energy greater than 120 to 192 meV.

7 Dynamic nanotube-adsorbate model

In Section 7.1 it was demonstrated that the CNT defect densities are on the same order of magnitude as dopant densities in traditional commercial semiconductors. This lends casual plausibility to the notion that they play an important role as adsorbate acceptor sites and possibly contributed to the hypothesis that chemisorbed molecules at these defect sites is the cause of threshold voltage shifts in CNT-FETs, and further, that the quantity of defects determines the effective doping level of the CNT channel. The correlations presented in Section 6.4 clearly show that the lattice defects play no such determining role in determining the effective doping level.

The subsequent revelations in Section 7.2 and Section 7.3, in which collision rates and adsorption binding energies were discussed, further suggest that the gas sensitivity of CNT-FETs may not be attributable to a static dopant concentration model. If the CNT-FET were to be examined solely as a comparison between UHV and atmospheric states, a static adsorption model may seem plausible. However, given the collision rates for the intermediate pressure range ($1.47 \times 10^6 \text{ s}^{-1}$ at 3.0×10^{-4} Torr), it is clear that an adsorbed monolayer will form so as to make the intermediate indistinguishable from the low vacuum regime (1.0 Torr). Periodic measurements of the gate-source curves at various pressures show that threshold ranges are stable for weeks at a time. This observation is strictly incompatible with a static dopant model (though not necessarily independent of defect-enhanced adsorption).

A much more plausible mechanism is a dynamic adsorption-desorption model. Some fraction of excited electrons created by biasing the CNT-FET scatter off of the adsorbed O_2 molecules, desorbing them from the CNT surface. The incident flux of O_2 molecules results in a pressure-dependent adsorption rate. The balancing of these adsorption and desorption rates results in a steady-state dopant concentration which is characteristic of the operating pressure. That is, the change in dopant concentration (per unit area), n_d is governed by an expression of the following form:

$$N_T \frac{dn_d}{dt} = \nu N_{\text{O}_2} e^{-E_d/E_q} - s\phi N_L \quad (19)$$

Where N_T is the total number of adsorption candidate sites in the channel, N_L is

the number of such lattice sites available for adsorbates, N_{O_2} are the number of sites occupied by adsorbates, s is the sticking coefficient (a temperature-dependent adsorption probability), E_d is the desorption activation energy (approximately equal to the adsorbate binding energy in the case of physisorption), E_q is the energy of the charge carriers, ϕ is the molecular flux as defined by Equation 18, and ν is a pre-exponential frequency factor.

The first term containing the exponential is a modified version of the spontaneous thermal desorption equation [62,63]. In the thermal case, ν is a temperature-dependent coefficient which represents the vibrational frequency of surface adsorbed molecules, given by $\nu = k_B T/h$ (effectively the number of opportunities per second a molecule is likely experience a desorption event, approximately $6.25 \times 10^{12} \text{ s}^{-1}$ at room temperature). In the case of current-induced desorption, ν must be dependent upon I_{DS} instead, as the electrons are responsible for the desorption events. Another substitution made is E_q in place of the thermal energy quantity, $k_B T$. Again, as the desorption events are caused by electron-adsorbate scattering rather than thermal excitations, the energy supply to overcome E_d , is dependent upon the energy of the charge carriers and therefore must depend, in some manner, upon V_{DS} , the FET bias.

An important accompanying note is that the electronic transitions in the CNT, as viewed in the Katura plot (Figure 6b), are on the same order of magnitude of the physisorbed O_2 binding energies, indicating that there a wealth of potential relaxation states for the desorption-initiating electrons. This also provides a context for potential

chirality-dependent effects which would explain a lack of correlation between the threshold voltage shifts and both the defect density, and the CNT channel length. In a purely static adsorption model for the dopant concentration, a correlation with either would be observed.

It is also of great importance that this proposed model does not rule out the possibility that lattice defects play some role in adsorption of ambient gas molecules. Indeed, from a theoretical standpoint, it has been shown that defect sites facilitate adsorption [20]. However, the data from this correlative study (Figure 37) suggest that the defects are not the primary indicator of the threshold voltage shift (and thereby the dopant concentration).

If a future study were to find that the defects are the principal adsorption sites, the proposed model (Equation 19) could be modified such that N_T would represent the number of defects. In such a case, the terms ν and E_q , which are dependent upon device operation (and thereby CNT chirality), must play a dominant role in determining the desorption/adsorption equilibrium condition. Absent this fact, a correlation between threshold voltage shift and D/G ratio would have been observed in Section 6.4. In this way, the defect density could determine the maximum dopant density (which, as mentioned, is on a similar order of magnitude to bulk semiconductor dopant densities) while the gas molecule collisions and the electronic structure of the CNT determine the steady-state dopant concentration.

7 Charge traps and transport

Another concept of interest in the field of defects and dopants is deep-level trap states. Deep-level traps are spatially localized mid-gap electronic states, usually in the vicinity of defects or impurities. Excited charge carriers fall into these trap states and ultimately recombine with their corresponding opposing carrier non-radiatively by releasing a phonon (known as the Shockley-Read-Hall process) [60]. One indicator of deep-level trap states is a broadening of the transition between the “on” and “off” states observed in a gate-source curve (that is, a reduction in transconductance). As charge carriers are injected into the channel, a larger gate voltage must be applied to fill the gap states in order to reach saturation. In addition, the reduced occupancy caused by the presence of the trap states results in a downward shift of the Fermi level and can thereby the Schottky barrier, causing a shift in the threshold voltage.

This effect can be observed qualitatively in Figure 17d due to increased oxygen concentration (a slight decrease in the slope of the curve for $V_G > V_{Go}$ as the chamber pressure is increased). As the other computational methods already required computation of the transconductance in the thermionic emission regime (Section 5.3), extrapolation of Δg (with respect to pressure) for statistical analysis was a straightforward endeavor. These data showed that the average transconductances were 66.1, 59.0, and 37.1 nmhos for chamber pressures of 3.5×10^{-9} , 3.0×10^{-4} , and 1.0 Torr, respectively. Average percent changes in transconductance for each pressure transition were observed to be -10.7% and -37.1% (from lowest to highest pressure, with

83.3% of these changes in transconductance being negative). The correlation of the threshold broadening with the chamber pressure clearly indicates that the surface adsorbed oxygen are acting as charge traps, decreasing the transconductance.

Further, no correlation was observed between either the transconductance or the change in the transconductance and the defect density (at static chamber pressures), which indicates that the defects do not intrinsically provide deep trap states and that it's unlikely that a trapping effect at the defect sites is being enhanced by the adsorbed oxygen. Rather, the deep-level trap correlation with pressure could support the dynamic adsorption-desorption model, wherein the desorption of O_2 molecules is the energy transfer mechanism by which charge carriers recombine (non-radiatively). Photodesorption studies of CNTs have also noted that there is a strong case for a desorption mechanism induced by excited charge carrier production and recombination [70].

8 Conclusion

This study has shown that there is no observable statistical correlation between either threshold voltage shift, or change in effective Schottky barrier at CNT-electrode junctions, due to the presence of oxygen adsorbates and the lattice defect density of the CNT channel. This suggests that adsorption of ambient gas molecules onto CNT surface defects is not the principal mechanism for oxygen sensitivity of CNT-FETs.

Further, evaluating the change in transconductance with respect to chamber pressure provided evidence that oxygen molecules generate deep trap states in the CNT channel which are responsible for the corresponding threshold voltage shift. A dynamic adsorption-desorption model was proposed which allows for adsorption sensitivity, the potential for defect-enhanced adsorption effects, and the lack of correlation observed. A corresponding functional form for this model was also described. This model, which includes a charge carrier-induced desorption mechanism, suggests that there could be chirality-dependent effects which drive the variation in threshold voltage shifts observed between devices. In the process of this discovery, a variety of instrumentation and analytical developments have been made.

With respect to Raman spectroscopy, various software and hardware developments have allowed more complex polarization-dependent measurements to be made. Large scale map analysis was carried out using a custom Python library which can be adapted and applied to many other spectrum mapping applications. In addition, the hardware control of a half-wave plate provides opportunities for even greater develop-

ments in Raman mapping with the following adaptations: (1) Polarization mapping functionality: Incident polarization could be used as an additional parameter, extending the spectrum map into a data cube which provides the option of either mapping polarization-dependent effects or, alternatively, to integrate the data cube, providing a polarization-independent map. (2) Polarization-feedback mapping: By inserting an analysis function during acquisition of the polarization-dependent data cube, the polarization could be dynamically adjusted and a mapping routine could be crafted to follow polarization-dependent contours in the Raman map. This would increase spectrum intensity for polarization-sensitive materials such as CNTs by maintaining optimal polarization orientation and, in the process, reduce map acquisition time by following the projected polarization path.

The development of the MEPS was also a substantial achievement of this study. The MEPS presents a robust and adaptable platform for applying a large number of atmospheric stimuli to specimen while collecting a similar variety of measurements. While most measurements presented in this study which utilize the MEPS reproduce existing work (absent correlative Raman data), Section 8.2 outlines some existing and potential capabilities which may be used to measure previously unobserved phenomena.

8 Broader impact

In the field of gas sensors, the results of this study will have substantial impact for CNT- and graphene-based devices. Under the previously conceived mechanisms for the impact of oxygen on CNT-FET transport, control over the defect density of the channel would be critical. The results of this study indicate that tuning the defect density within reasonable limits will not improve or degrade detection limits of CNT-based (and likely graphene-based) sensors. The defect density of CNTs and graphene can be tuned to some degree during the growth by varying the ratio between the carbon feedstock and reducing species gases, or alternatively, by post-processing via ion bombardment. Eliminating the defect density as a parameter of interest can guide researchers and engineers in their endeavor to optimize these carbon-based sensors.

Development and modeling of next generation CNT-based electron field emission sources may also benefit from the conclusions of this study. Due to their high aspect ratio and ease of vertical alignment, CNTs show promise as electron filaments. One major concern in extending emitter lifetime is surface contamination. In this sense, developing a better understanding of the mechanisms for gas adsorption will contribute greatly towards developing models for, and protocols to extend, emitter lifetime. In addition, characterizing the mechanisms behind ambient gas sensitivity will inform emitter design and fabrication. For instance, by tuning the chirality of the CNT emitter so as to reduce any variation in emission threshold due to trace gas contaminants.

With respect to the field of CNTs and graphene in general, the defect quantification methods presented provide an opportunity for advancing measurement protocols. Introducing the D/G ratio histogram as a new standard for defect density characterization may be advantageous. The vast majority of studies which concern CNT defect densities in some fashion rely solely on a single spectrum to characterize the entire channel. It is immediately apparent, upon inspecting the D/G ratio histograms (Figure 32), that this is a wholly inadequate extrapolation. A comprehensive assessment of defect density must include some notion as to amount of variation throughout the specimen, which is provided directly in the D/G ratio histogram.

8 Further studies

While the present study has offered a number of new insights to the field of CNT-FET gas sensors, there are additional avenues to broaden impact of this study and provide a deeper understanding of any CNT-adsorbate phenomena. Beyond simply increasing the statistical population of devices, three possible expansions are offered.

8.2.1 Differentiation: metallic vs. semiconducting

As previously mentioned in Section 2.1, a subset of chiralities have energy bands at the Fermi level, resulting in a hybrid of conductor and semiconductor characteristics. Some computational efforts by Kang et al. [53,54] suggest that the adsorption of O₂ molecules to the surface of a CNT results in the creation of additional states near the

Fermi level. The presence of pre-existing mid-gap states in the metallic CNTs may result in a different trend than those which are semiconducting. Specifically, smaller changes in the Schottky barrier shift, or perhaps other more dominant secondary effects (less change in transconductance due to the charge traps).

8.2.2 Photostimulated transport

In recent years, photonic stimulation and photo-emission spectroscopy of CNT-FETs have been of interest to researchers [71–74]. By measuring the gate-source characteristics while irradiating the CNT channel with a tunable IR source, it has been shown that the chirality of the CNT can be determined by correlating a peak in photocurrent with the wavelength of the excitation source. However, these studies have only been carried out under atmospheric conditions. In addition, none have considered the effects of the photonic stimulation on the back-gate substrate, conductively doped silicon, which could increase the local charge density and thereby mimic a change in gate voltage. In the process of this study, the MEPS system was fitted with a fiber optic feed-through and tunable IR source Figure 38, making it the ideal tool to address these issues.

Figure 38: (a) Cross-section of custom feed-through with Teflon ferrule. Photographs of (a) optical fiber feed-through and (b) clamping fiber armature above a specimen.

8.2.3 Kelvin probe measurements

With the work function of electrode materials being such a critical factor in device performance (being responsible in part for determining the Schottky barrier height), it stands to reason that a simultaneous *in situ* work function measurement would be beneficial. In this way, effects due to fluctuations in the source and drain electrodes could be subtracted and result in a pure measurement of the CNT channel. This could be achieved by allocating a probe port with a Kelvin probe (Figure 39). The accompanying schematic (Figure 39b) shows how an AC signal, $V(t)$ can be applied in a decoupled fashion to drive the the probe with a height adjustment potential, U_1 . The induced current, fed through a lock-in amplifier and integrator, can be read out on an ammeter. The compensating potential, U_2 , can then be adjusted to reduce the measured current to zero. At which point, U_2 will be equal to the difference in work function between the probe and the measured specimen.

Figure 39: Schematic of (a) Kelvin probe feed-through and (b) control and measurement electronics.

References

- [1] S. Iijima, *Nature*, 1991, **354**, 56–58.
- [2] S. Saito, *Science*, 1997, **278**, 77–78.
- [3] A. Naeemi, J. D. Meindl, *Annual Review of Materials Research*, 2009, **39**, 255–275.
- [4] J. Y. Huang, S. Chen, Z. Q. Wang, K. Kempa, Y. M. Wang, S. H. Jo, G. Chen, M. S. Dresselhaus, Z. F. Ren, *Nature*, 2006, **439**, 281–281.
- [5] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer, R. E. Smalley, *Science*, 1996, **273**, 483–487.
- [6] K. Chu, Q. Wu, C. Jia, X. Liang, J. Nie, W. Tian, G. Gai, H. Guo, *Composites Science and Technology*, 2010, **70**, 298 – 304.
- [7] A. K.-T. Lau, D. Hui, *Composites Part B: Engineering*, 2002, **33**, 263 – 277.
- [8] J. Wang, *Electroanalysis*, 2005, **17**, 7–14.
- [9] J.-M. Bonard, J.-P. Salvetat, T. Stöckli, W. A. d. Heer, L. Forró, A. Châtelain, *Applied Physics Letters*, 1998, **73**, 918–920.
- [10] W. Zhu, C. Bower, O. Zhou, G. Kochanski, S. Jin, *Applied Physics Letters*, 1999, **75**, 873–875.
- [11] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, H. Dai, *Science*, 1999, **283**, 512–514.
- [12] G. Pirio, P. Legagneux, D. Pribat, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, *Nanotechnology*, 2002, **13**, 1.
- [13] J. I. Sohn, S. Lee, Y.-H. Song, S.-Y. Choi, K.-I. Cho, K.-S. Nam, *Applied Physics Letters*, 2001, **78**, 901–903.
- [14] D. H. Lee, J. E. Kim, T. H. Han, J. W. Hwang, S. Jeon, S.-Y. Choi, S. H. Hong, W. J. Lee, R. S. Ruoff, S. O. Kim, *Advanced Materials*, 2010, **22**, 1247–1252.
- [15] J. Li, Q. Ye, A. Cassell, H. T. Ng, R. Stevens, J. Han, M. Meyyappan, *Applied Physics Letters*, 2003, **82**, 2491–2493.
- [16] S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, P. Avouris, *Physical Review Letters*, 2002, **89**.
- [17] A. Javey, J. Guo, Q. Wang, M. Lundstrom, H. Dai, *supernovae*, 1999, **118**, 1766–1776.

- [18] P. G. Collins, *Science*, 2000, **287**, 1801–1804.
- [19] D. McClain, N. Thomas, S. Youkey, R. Schaller, J. Jiao, K. P. O’Brien, *Carbon*, 2009, **47**, 1493–1500.
- [20] N. Govind, J. Andzelm, A. Maiti, *IEEE Sensors Journal*, 2008, **8**, 837–841.
- [21] M. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, *Physics Reports*, 2005, **409**, 47–99.
- [22] M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus, R. Saito, *Nano Letters*, 2010, **10**, 751–758.
- [23] V. N. Popov, P. Lambin, *Physica Status Solidi B*, 2009, **246**, 2602–2605.
- [24] G. S. Duesberg, I. Loa, M. Burghard, K. Syassen, S. Roth, *Physical review letters*, 2000, **85**, 5436–5439.
- [25] A. M. Rao, A. Jorio, M. A. Pimenta, M. S. S. Dantas, R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical review letters*, 2000, **84**, 1820–1823.
- [26] M. S. Dresselhaus, A. Jorio, A. G. Souza Filho, R. Saito, *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 2010, **368**, 5355–5377.
- [27] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, *Nature*, 2005, **438**, 197–200.
- [28] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, *Proceedings of the National Academy of Sciences of the United States of America*, 2005, **102**, 10451–10453.
- [29] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Rev. Mod. Phys.*, 2009, **81**, 109–162.
- [30] J.-H. Chen, W. G. Cullen, C. Jang, M. S. Fuhrer, E. D. Williams, *Physical review letters*, 2009, **102**, 236805.
- [31] E. H. Martins Ferreira, M. V. O. Moutinho, F. Stavale, M. M. Lucchese, R. B. Capaz, C. A. Achete, A. Jorio, *Phys. Rev. B*, 2010, **82**, 125429.
- [32] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, L. Wirtz, *Nano Letters*, 2007, **7**, 238–242.
- [33] R. Saito, M. Fujita, G. Dresselhaus, M. S. Dresselhaus, *Applied Physics Letters*, 1992, **60**, 2204–2206.

- [34] H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, Y. Achiba, *Synthetic Metals*, 1999, **103**, 2555–2558.
- [35] R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Review B*, 2000, **61**, 2981.
- [36] J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, P. Ordejón, *Phys. Rev. Lett.*, 2004, **92**, 075501.
- [37] J. Maultzsch, S. Reich, C. Thomsen, *Physical Review B*, 2004, **70**, 155403.
- [38] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, A. K. Geim, *Physical Review Letters*, 2006, **97**.
- [39] F. Tuinstra, *The Journal of Chemical Physics*, 1970, **53**, 1126.
- [40] I. Pócsik, M. Hundhausen, M. Koós, L. Ley, *Journal of Non-Crystalline Solids*, 1998, **227–230**, Part 2, 1083 – 1086.
- [41] C. Thomsen, S. Reich, *Phys. Rev. Lett.*, 2000, **85**, 5214–5217.
- [42] A. Ferrari, *Solid State Communications*, 2007, **143**, 47–57.
- [43] K. Sato, R. Saito, Y. Oyama, J. Jiang, L. Cancado, M. Pimenta, A. Jorio, G. Samsonidze, G. Dresselhaus, M. Dresselhaus, *Chemical Physics Letters*, 2006, **427**, 117–121.
- [44] R. Saito, T. Takeya, T. Kimura, G. Dresselhaus, M. S. Dresselhaus, *Physical Review B*, 1998, **57**, 4145.
- [45] A. Jorio, M. A. Pimenta, A. G. Souza Filho, R. Saito, G. Dresselhaus, M. S. Dresselhaus, *New Journal of Physics*, 2003, **5**, 139.
- [46] W. Shockley, *Electrons and Holes in Semiconductors: With Applications to Transistor Electronics*, of *The Bell Telephone Laboratories series*, D. Van Nostrand, 1959.
- [47] E. Rhoderick, R. Williams, *Metal semiconductor contacts*, 2nd. Edn., Oxford university press, 1988.
- [48] C. Casiraghi, A. Hartschuh, H. Qian, S. Piscanec, C. Georgi, A. Fasoli, K. S. Novoselov, D. M. Basko, A. C. Ferrari, *Nano Letters*, 2009, **9**, 1433–1441.
- [49] M. Lucchese, F. Stavale, E. M. Ferreira, C. Vilani, M. Moutinho, R. B. Capaz, C. Achete, A. Jorio, *Carbon*, 2010, **48**, 1592–1597.

- [50] L. G. Cancado, A. Jorio, E. H. M. Ferreira, F. Stavale, C. A. Achete, R. B. Capaz, M. V. O. Moutinho, A. Lombardo, T. S. Kulmala, A. C. Ferrari, *Nano Letters*, 2011, **11**, 3190–3196.
- [51] A. Jorio, R. Saito, J. H. Hafner, C. M. Lieber, M. Hunter, T. McClure, G. Dresselhaus, M. S. Dresselhaus, *Physical Review Letters*, 2001, **86**, 1118–1121.
- [52] K. Besocke, S. Berger, *Review of Scientific Instruments*, 1976, **47**, 840–842.
- [53] D. Kang, N. Park, J. Hyun, E. Bae, J. Ko, J. Kim, W. Park, *Applied Physics Letters*, 2005, **86**, 093105.
- [54] D. Kang, N. Park, J. Ko, E. Bae, W. Park, *Nanotechnology*, 2005, **16**, 1048.
- [55] K. Bradley, J.-C. P. Gabriel, M. Briman, A. Star, G. Gruner, *Physical Review Letters*, 2003, **91**.
- [56] S. Dag, O. Gülseren, T. Yildirim, S. Ciraci, *Phys. Rev. B*, 2003, **67**, 165424.
- [57] A. Tchernatinsky, S. Desai, G. U. Sumanasekera, C. S. Jayanthi, S. Y. Wu, B. Nagabhirava, B. Alphenaar, *Journal of Applied Physics*, 2006, **99**, 034306.
- [58] M. Hatami, A. Farmany, R. Sahraei, *Fullerenes, Nanotubes and Carbon Nanostructures*, 2014, **22**, 434–453.
- [59] H. Chang, J. D. Lee, S. M. Lee, Y. H. Lee, *Applied Physics Letters*, 2001, **79**, 3863–3865.
- [60] D. K. Schroder, *Semiconductor material and device characterization*, John Wiley & Sons, 2006.
- [61] L. G. Cancado, K. Takai, T. Enoki, M. Endo, Y. A. Kim, H. Mizusaki, A. Jorio, L. N. Coelho, R. Magalhaes-Paniago, M. A. Pimenta, *Applied Physics Letters*, 2006, **88**, 163106.
- [62] J. M. Lafferty, L. G. Rubin, *Foundations of vacuum science and technology*, AIP, 1999.
- [63] M. H. Hablanian, *High-vacuum technology: a practical guide, Vol. 111*, CRC Press, 1997.
- [64] A. Kutana, K. P. Giapis, *The Journal of Physical Chemistry C*, 2009, **113**, 14721–14726.
- [65] R. E. Palmer, P. J. Rous, J. L. Wilkes, R. F. Willis, *Phys. Rev. Lett.*, 1988, **60**, 329–332.

- [66] P. H. Krupenie, *Journal of physical and chemical reference data*, 1972, **1**, 423–534.
- [67] G. J. Schulz, *Rev. Mod. Phys.*, 1973, **45**, 423–486.
- [68] M. J. Bojan, W. A. Steele, *Langmuir*, 1987, **3**, 1123–1127.
- [69] H. Ulbricht, G. Moos, T. Hertel, *Physical Review B*, 2002, **66**.
- [70] R. J. Chen, N. R. Franklin, J. Kong, J. Cao, T. W. Tombler, Y. Zhang, H. Dai, *Applied Physics Letters*, 2001, **79**, 2258.
- [71] J. A. Misewich, *Science*, 2003, **300**, 783–786.
- [72] M. Freitag, V. Perebeinos, J. Chen, A. Stein, J. C. Tsang, J. A. Misewich, R. Martel, P. Avouris, *Nano Letters*, 2004, **4**, 1063–1066.
- [73] M. Freitag, Y. Martin, J. A. Misewich, R. Martel, P. Avouris, *Nano Letters*, 2003, **3**, 1067–1071.
- [74] X. Qiu, M. Freitag, V. Perebeinos, P. Avouris, *Nano Letters*, 2005, **5**, 749–752.

Appendix A Python code

A Classes

The following defined classes were compiled into a library for the analysis procedures discussed in this manuscript. They were accompanied with the following import header:

```
1 # General computational package
2 import numpy
3
4 # File I/O and parsing packages
5 import sys
6 import csv
7
8 # Curve fitting package
9 import lmfit
10 from lmfit.models import *
11
12 # Plotting packages
13 import matplotlib.pyplot as pyplot
14 import matplotlib as matplot
15 from matplotlib import cm
```

A.1.1 CNTFET

Main wrapper for containing all MEPS and Raman data as well as general metadata concerning the device. This class need only be instantiated once for an entire pool of devices.

```
1 class CNTFET:
2
3     def __init__(self, device="n.m.x", runs=[1,2,3]):
4
5         # Device information
6         self.name = str(device)
7         self.runs = [int(i) for i in runs]
8
9         # Initialize dict of MEPS runs
10        self.meps = {}
11        self.raman = None
12        self.gateplots = None
13
14        # Load MEPS data into CNT-FET
```



```

15 def load_meps(self, path="", pressure=3.5e-9):
16     if pressure < 5e-8: vac = 'uhv'
17     elif pressure < 5e-4: vac = 'hv'
18     elif pressure < 5e-2: vac = 'lv'
19     else: vac = 'atm'
20     self.meps[vac] = {}
21     for i in self.runs:
22         filename = self.name + "_" + str(i) + ".csv"
23         self.meps[vac][i] = MEPS(run=i, pressure=pressure)
24         self.meps[vac][i].load(path=path, filename=filename)
25
26 # Set runs, required for loading multiple pressure values
27 def set_runs(self, runs=[1,2,3]):
28     self.runs = [int(i) for i in runs]

```

A.1.2 MEPS

Contains MEPS data. Multiple gate sweep runs can be stored in a single instance of this class but are considered trials with identical settings. This class must be instantiated for each pressure setting.

```

1 class MEPS:
2
3     def __init__(self, pressure=3.5e-9, run=1, vds=numpy.arange(-1,-
4         1+9*0.25,0.25, dtype=float)):
5
6         # Chamber pressure during measurement
7         self.pressure = float(pressure)
8         self.vds = vds
9         self.data = {}
10        self.plot = {}
11
12        # Contents of data file (initialize)
13        self.datafile = str("")
14        self.filename = str("")
15        self.filepath = str("")
16        self.run = int(run)
17
18        # Manually set Vds value
19        def set_vds(self, vds):
20            self.vds = numpy.array(vds, dtype=float)
21
22        # Load

```

```

22 def load(self, path="", filename="", delim=","):
23
24     # Store file info
25     self.filename = str(filename)
26     self.filepath = str(path)
27
28     # Comment filtering function
29     def filtercomment(iterator):
30         for line in iterator:
31             if line[:1].isalpha() or line[:1]=="#": continue
32             if not line.strip(): continue
33             yield line
34
35     # Store raw text of datafile for later parsing
36     with open(path+filename, 'rb') as f: self.datafile = f.read()
37     with open(path+filename, 'rb') as f:
38         # Read data in file
39         reader = csv.reader(filtercomment(f), delimiter=delim)
40         xyvals = list(reader)
41
42     # First two numerical points describe the number of data points
43     # Vg / Ids value pairs
44     xpoints = int(xyvals[0][0])
45     # Vds values (number of Vg sweeps)
46     sweeps = int(xyvals[1][0])
47
48     # Collect Vds data from configuration header
49     for line in self.datafile.split("\r\n"):
50         line = line.split(",")
51         if line[0] == "Test_Parameter":
52             if line[1] == "Measurement.Secondary.Start": vdso = float(
                    line[2])
53             if line[1] == "Measurement.Secondary.Count": vdsi = int(line[
                    2])
54             if line[1] == "Measurement.Secondary.Step": vdsd = float(line
                    [2])
55     # Numpy array of Vds values
56     self.vds = numpy.arange(vdso, vdso + vdsi*vdsd, vdsd, dtype=
        float)
57
58     # Extract x-y values of gate sweep
59     xyvals = numpy.transpose(numpy.array(xyvals[2:], dtype=float))

```

```

60 xvals = numpy.array_split(xyvals[0],sweeps)
61 yvals = numpy.array_split(xyvals[1],sweeps)
62
63 # Iterate over each sweep (number of Vds values) and store data
64 for i in range(0,vdsi):
65     self.data[self.vds[i]] = GateSweep(xdata=xvals[i], ydata=yvals
66         [i], vds=self.vds[i])
67     # Compute useful statistics for each sweep and store
68     self.data[self.vds[i]].calc_ids_stats()
69
70 # Create and store a plot of the run
71 def plot_gatesweep(self, xlabel="$V_{G}$$(V)$", ylabel="$I_{DS}$",
72     title=None, devname=None, showstats=False):
73
74     # Initialize
75     outplot = pyplot.figure(figsize=(10,8))
76     pyplot.tick_params(axis='both', which='major', labelsize=16)
77
78     # Determine yscale
79     idsmax = max(self.data[self.vds[-1]].ids)
80     orders = { 15:'f', 12:'p', 9:'n', 6:'\mu', 3:'m', 1:'' }
81     for i in sorted(orders.keys())[::-1]:
82         if idsmax*(10**float(i)) >= 1.0 : units,mag='_'$(''+orders[i]+'_'
83             A)$',i
84
85     # Labels and titles
86     pyplot.xlabel(str(xlabel), fontsize=16)
87     pyplot.ylabel(str(ylabel+units), fontsize=16)
88     if devname != None and title == None: title = str(devname)
89     if title == None: pyplot.title('(Run_'+str(self.run)+')',
90         fontsize=18)
91     else: pyplot.title(str(title)+'_(Run_'+str(self.run)+')',
92         fontsize=18)
93
94     # Plot each gate sweep (Vds value)
95     for vds in self.vds:
96         pyplot.plot(self.data[vds].vg, self.data[vds].ids*(10**float(
97             mag)), color='blue')
98
99     if showstats == True:
100         for vds in self.vds:

```

```

95     stats = [self.data[vds].imin, self.data[vds].pmax, self.data[
vds].nmax]
96     for stat in stats:
97         if stat != None: pyplot.plot(stat[0], stat[1]*(10**float(mag
)), 'o', color='red')
98     if self.data[1.0].pthresh != None:
99         for point in self.data[1.0].pthresh.values():
100             pyplot.plot(point[0], point[1]*(10**float(mag)), 'o', color=
'green')
101     if self.data[1.0].nthresh != None:
102         for point in self.data[1.0].nthresh.values():
103             pyplot.plot(point[0], point[1]*(10**float(mag)), 'o', color=
'green')
104
105     self.plot = outplot
106     pyplot.close()

```

A.1.3 GateSweep

Contains a single gate sweep curve (i.e. I_{DS} vs. V_G at fixed V_{DS}). Also defines data analysis routines and stores important computed quantities. This class is automatically instantiated by the MEPS class.

```

1 class GateSweep:
2
3     def __init__(self, xdata=None, ydata=None, vds=0.0):
4
5         # Collection quantities
6         # Drain-source bias
7         self.vds = float(vds)
8         # Data arrays: D-S current, G bias
9         self.ids = numpy.array(ydata)
10        self.vg = numpy.array(xdata)
11
12        # Computed quantites
13        # Threshold voltages
14        self.pthresh = None
15        self.nthresh = None
16        self.psubthresh = None
17        self.nsubthresh = None
18        # D-S current maxima and minimum
19        self.imin = None
20        self.pmax = None

```

```

21     self.nmax = None
22     # On/off ratio
23     self.ponoff = None
24     self.nonoff = None
25     # Thermionic emission data
26     self.thermrange = None
27     self.thermfit = None
28     self.vgknee = None
29
30     # Minor functions to set x/y values
31     def set_x(self, xvals):
32         self.vg = numpy.array(xvals)
33     def set_y(self, yvals):
34         self.ids = numpy.array(yvals)
35
36     # Find index of a value in a numpy array
37     def getindex(x, target):
38         return numpy.abs(x - target).argmin()
39
40     # Compute Ids max/min and on/off ratios
41     def calc_ids_stats(self):
42
43         # Calculate Ids min point
44         index = numpy.abs(self.ids).argmin()
45         self.imin = [self.vg[index], self.ids[index], index]
46
47         # Calculate Ids max points (p-type)
48         if self.imin[2] == 0: index = 0
49         else: index = numpy.abs(self.ids[:self.imin[2]]).argmax()
50         self.pmax = [self.vg[index], self.ids[index], index]
51
52         # Calculate Ids max points (n-type)
53         if self.imin[2] == len(self.ids)-1: index = len(self.ids)-1
54         else: index = numpy.abs(self.ids[self.imin[2]:]).argmax() +
55             self.imin[2]
56         self.nmax = [self.vg[index], self.ids[index], index]
57
58         # Calculate on/off ratio with divide-by-zero exception
59         if self.imin[1] == 0.0: self.ponoff, self.nonoff = numpy.nan,
60             numpy.nan
61         else: self.ponoff, self.nonoff = self.pmax[1]/self.imin[1],
62             self.nmax[1]/self.imin[1]

```

```

60
61 # Compute threshold and sub-threshold voltages
62 def calc_thresh(self, transport=None):
63
64     if transport.lower() == 'p':
65         # p-type transport
66         # Compute 1/e points for Ids
67         idslow = self.imin[1] + numpy.exp(-1)*(self.pmax[1] - self.
            imin[1])
68         idshigh = self.pmax[1] - numpy.exp(-1)*(self.pmax[1] - self.
            imin[1])
69
70         # Locate array index for 1/e points
71         plow = numpy.abs(self.ids[self.pmax[2]:self.imin[2]] - idslow)
            .argmin()
72         phigh = numpy.abs(self.ids[self.pmax[2]:self.imin[2]] -
            idshigh).argmin()
73
74         # Save threshold and sub-threshold values [Vg, Ids, index]
75         self.pthresh = { 'low':[self.vg[plow],self.ids[plow],plow], '
            high':[self.vg[phigh],self.ids[phigh],phigh] }
76
77     if transport == 'n':
78         # n-type transport
79         # Compute 1/e points for Ids
80         idslow = self.imin[1] + numpy.exp(-1)*(self.nmax[1] - self.
            imin[1])
81         idshigh = self.nmax[1] - numpy.exp(-1)*(self.nmax[1] - self.
            imin[1])
82
83         # Locate array index for 1/e points
84         nlow = numpy.abs(self.ids[self.imin[2]:self.nmax[2]] - idslow)
            .argmin() + self.imin[2]
85         nhigh = numpy.abs(self.ids[self.imin[2]:self.nmax[2]] -
            idshigh).argmin() + self.imin[2]
86
87         # Save threshold and sub-threshold values [Vg, Ids, index]
88         self.pthresh = { 'low':[self.vg[nlow],self.ids[nlow],nlow], '
            high':[self.vg[nhigh],self.ids[nhigh],nhigh] }
89
90 # Fit a specified window of gate sweep

```

```

91 def gatesweep_linear_fit(self, fitrange=None, slope=None,
    intercept=None):
92
93     # Select data only in desired range
94     if fitrange == None:
95         xvals = self.vg
96         yvals = self.ids
97     else:
98         xvals = self.vg[fitrange[0]:fitrange[1]]
99         yvals = self.ids[fitrange[0]:fitrange[1]]
100
101     # Create linear model
102     fit_model = BackgroundModel()
103     fit_params = fit_model.make_params()
104
105     # Update initial parameters
106     if slope == None: slope = (yvals[-1] - yvals[0])/(xvals[-1] -
        xvals[0])
107     if intercept == None: intercept = numpy.average(yvals) - slope*
        numpy.average(xvals)
108     fit_params['a'].set(slope)
109     fit_params['b'].set(intercept)
110
111     # Compute Fit
112     fit_out = fit_model.fit(yvals, params=fit_params, x=xvals,
        method="leastsq")
113
114     # Return slope, y-intercept, and "x-intercept" (only valid for
        voltage knee of full sweep)
115     slope = fit_out.params['a']._val
116     yint = fit_out.params['b']._val
117     xint = (numpy.min(self.ids)-fit_out.params['b']._val)/fit_out.
        params['a']._val
118     rsq = 1.0 - fit_out.residual.var() / numpy.var(yvals)
119     return [slope, yint, xint, rsq]
120
121     # Find thermionic regime of sweep and fit
122     def fit_thermionic(self, slopethresh=0.9, chans=20):
123
124         slopelist = []
125         for i in range(0,len(self.vg)-chans):
126

```

```

127     # Fit segment of gatesweep
128     fitrange = [i,i+chans]
129     fitdata = self.gatesweep_linear_fit(fitrange=fitrange)
130     slopelist.append(fitdata[0])
131
132     # Compute indices of thermionic range in terms of xdata, ydata
133     (full sweep)
134     slopelist = numpy.array(slopelist)
135     therm_indices = numpy.where(slopelist > slopethresh*max(
136         slopelist))[0]
137     therm_range = [therm_indices[0]+int(chans/2), therm_indices[-1
138         ]+int(chans/2)]
139
140     thermionicdata = self.gatesweep_linear_fit(fitrange=therm_range
141         )
142     self.thermrange = therm_range
143     self.thermfit = thermionicdata[0:1] + thermionicdata[-1]
144     self.vgknee = thermionicdata[2]

```

A.1.4 Raman

Contains a single Raman map for analysis. Does not perform map stitching operations. Contains all routines for region identification and statistical analysis.

```

1 class Raman:
2
3     def __init__(self, device=None, filepath=None, filename=None,
4         delim='\t'):
5
6         self.device = device
7         self.mapdata = None
8         self.xvals = None
9
10        # Region classification (component names, spectra, classified
11        spectra)
12        self.spectypes = None
13        self.thresh = None
14        self.cntcoeffs = None
15        self.regionspectra = {}
16        self.regionmap = {}
17        self.regionstats = {}
18
19        # Quantification

```



```

18     self.mapstats = {}
19
20     # Visualization
21     self.plots = {}
22
23     # Load map data directly if paths are provided
24     if filepath != None and filename != None:
25         self.load_data(filepath, filename, delim)
26
27     # Load map data
28     def load_data(self, filepath, filename, delim='\t'):
29
30         # Read map data
31         mapdata = list()
32         with open(filepath + filename, 'rb') as f:
33             for line in f:
34                 # Ignore comment lines
35                 if line[:1] == "#": continue
36                 # Spectrum x-values contained in lines which begin with
37                 # delimiter
38                 if line[:1] == delim: xvals = numpy.array(line.strip().split(
39                     delim), dtype=float)
40                 # All other lines are x,y and spectrum intensity values
41                 else:
42                     xy = numpy.array(line.split(delim)[:2], dtype=float)
43                     spec = numpy.array(line.split(delim)[2:], dtype=float)
44                     # Shift spectrum if any intensity is sub-zero
45                     if min(spec) < 100.0: spec = spec + (100 - min(spec))
46                     mapdata.append(numpy.array([xy, spec]))
47             # Cleanup for loading data
48             f.close()
49             self.mapdata = numpy.array(mapdata)
50             self.xvals = xvals
51
52     # Load lookup spectra for region identification
53     def load_lookup(self, filepath, delim='\t', spectypes=[
54         'background', 'edge', 'electrode', 'cnt']):
55
56     # Load spectra lookup table
57     self.spectypes = spectypes
58     for region in spectypes: self.regionmap[region] = list()

```

```

57 # Iterate over list of spectrum types
58 for region in spectypes:
59     with open(filepath + region + '.xy', 'rb') as f:
60         reader = csv.reader(f, delimiter=delim)
61         spectrum = list(reader)
62     f.close()
63     # Push spectrum to dict
64     self.regionspectra[region] = numpy.transpose(numpy.array(
        spectrum, dtype=float))
65
66 # Compute correlation coefficient for map spectra and classify
    into regions
67 def classify_regions(self, thresh=0.75):
68
69     # Init cross-correlation coeff tracking
70     coefftracker = {}
71     for regionname in self.regionmap.keys(): coefftracker[
        regionname] = []
72
73     # Deprecated
74     self.thresh = thresh
75
76     # Iterate over all points in map for region classification
77     for point in self.mapdata:
78         # Compute correlation coefficient between spectra and lookup
            table
79         regioncoeffs = {}
80         for region in self.spectypes:
81             regioncoeffs[region] = self.xcorrelate(point[1], self.
                regionspectra[region][1])
82         # Determine best region match
83         regionname = self.bestregion(regioncoeffs)
84         coefftracker[regionname].append(regioncoeffs[regionname])
85         self.regionmap[regionname].append(point)
86
87     # Assess cut-off for CNT region
88     if len(coefftracker['cnt']) > 0:
89         thresh = (1-numpy.exp(-1))*max(coefftracker['cnt'])
90         self.regionmap['cnt'] = numpy.array(self.regionmap['cnt'])[
            numpy.where(numpy.array(coefftracker['cnt']) > thresh)]
91         self.cntcoeffs = numpy.array(coefftracker['cnt'])[numpy.where(
            numpy.array(coefftracker['cnt']) > thresh)]

```

```

92
93 # Compute/print region statistics/classifications
94 def show_regionstats(self):
95
96     # Classify/compute if not already completed
97     if len(self.regionmap.keys()) == 0 : self.classify_regions()
98     if len(self.regionstats.keys()) == 0:
99         for region in self.spectypes:
100             self.regionstats[region] = len(self.regionmap[region])
101             self.regionstats['classified'] = sum([len(i) for i in self.
regionmap.values()])
102             self.regionstats['total'] = len(self.mapdata)
103             self.regionstats['unclassified'] = self.regionstats['total'] -
self.regionstats['classified']
104
105     # Print stats for spectra in various classifications
106     for region in self.spectypes:
107         print region + '\t' , str(self.regionstats[region])
108
109     # Print totals
110     print 'classified' + '\t' , str(self.regionstats['classified'])
111     print 'unclassified' + '\t' , str(self.regionstats['
unclassified'])
112     print 'total' + '\t' , str(self.regionstats['total'])
113     print 'thresh' + '\t' , str(self.thresh)
114
115     # Export xy data of points which are in each region (no quant/
spectrum)
116 def export_regionmap(self, filepath, regions=None):
117
118     # Regions to export
119     if regions == None: regions = self.spectypes
120     else: regions = list(regions)
121
122     # Iterate over regions
123     for region in regions:
124         # Write to file: region-points-(threshold).xy
125         with open(filepath + self.device + '-' + str(region) + '-
points-( ' + str(thresh) + ').xy', 'w') as f:
126             for point in self.regionmap[region]:
127                 x = point[0][0]
128                 y = point[0][1]

```

```

129     message = str(x)+"\t"+str(y)+"\n"
130     f.write(message)
131     f.close()
132
133     # Compute spectrum stats for CNT region
134     def calc_stats(self):
135
136         # List of stats, initialize dumping ground for stats, peak
137         # windows
138         statlist = ["x", "y", "D", "G", "2D", "D/G"]
139         for stat in statlist: self.mapstats[stat] = list()
140         drange = [1280.0, 1410.0]
141         grange = [1510.0, 1670.0]
142         gprange = [2620.0, 2760.0]
143
144         # Compute integrated intensity of D, G, and 2D peaks
145         for point in self.regionmap["cnt"]:
146
147             dintensity = numpy.sum(self.get_peak(xdata=self.xvals, ydata=
148             point[1], peakname='D'))
149             gintensity = numpy.sum(self.get_peak(xdata=self.xvals, ydata=
150             point[1], peakname='G'))
151             gpintensity = numpy.sum(self.get_peak(xdata=self.xvals, ydata=
152             point[1], peakname='2D'))
153
154             self.mapstats["x"].append(point[0][0])
155             self.mapstats["y"].append(point[0][1])
156             self.mapstats["D"].append(dintensity)
157             self.mapstats["G"].append(gintensity)
158             self.mapstats["2D"].append(gpintensity)
159             self.mapstats["D/G"].append(dintensity/gintensity)
160
161         # Export CNT stats for each data point in CNT region
162         def export_cntstatmap(self, filepath):
163
164             statlist = ["x", "y", "D", "G", "2D", "D/G"]
165             with open(filepath + self.device + '-' + 'cnt-stats.xyz', 'w')
166                 as f:
167                 f.write('#' + '\t'.join(statlist) + '\n')
168                 for i in range(0, len(self.mapstats[statlist[0]])):
169                     f.write('\t'.join(str(self.mapstats[stat][i]) for stat in
170                     statlist) + '\n')

```

```

165     f.close()
166
167     # Plot a map of the CNT region
168     def plot_map(self, stats=None):
169
170         if stats == None: stats = ["D", "G", "2D", "D/G"]
171         else: stats = list(stats)
172
173         x = numpy.array(self.mapstats["x"], dtype=float)
174         y = numpy.array(self.mapstats["y"], dtype=float)
175
176         # Window of plot
177         xspan = numpy.array([ int(round(min(x)-0.5)) , int(round(0.5 +
178             max(x))) ], dtype=int)
179         yspan = numpy.array([ int(round(min(y)-0.5)) , int(round(0.5 +
180             max(y))) ], dtype=int)
181
182         # Increase size of abnormally small maps
183         if xspan[1]-xspan[0] < 20:
184             dx = int(round((21.0 - (xspan[1]-xspan[0]))/2.0))
185             xspan += numpy.array([-dx,dx])
186         if yspan[1]-yspan[0] < 20:
187             dy = int(round((21.0 - (yspan[1]-yspan[0]))/2.0))
188             yspan += numpy.array([-dy,dy])
189         plotsize = [ (xspan[1]-xspan[0])/2.0, (yspan[1]-yspan[0])/2.0]
190
191         # Generate plots for each type of stat requested
192         for stat in stats:
193
194             # Z values (color)
195             z = numpy.array(self.mapstats[stat], dtype=float)
196
197             # Determine order of magnitude of max point, minimum 10^0
198             logzmax = max([round(numpy.log10(max(z)) + 0.5), 0.0])
199             logzmin = max([round(numpy.log10(min(numpy.abs(z))) - 0.5), -3
200                 ])
201
202             # Color scale mapping
203             norm = matplotlib.colors.LogNorm(vmax=10**logzmax, vmin=10**
204                 logzmin)
205
206             # Plot formatting

```

```

203     outplot = pyplot.figure(figsize=(plotsize[0],plotsize[1]))
204     pyplot.axis(numpy.hstack([xspan,yspan]))
205     pyplot.title(self.device + '_( ' + stat + ' )', fontsize=18)
206     pyplot.xlabel('$x$_{($\mu_m$)}', fontsize=16)
207     pyplot.ylabel('$y$_{($\mu_m$)}', fontsize=16)
208     pyplot.tick_params(axis='both', which='major', labelsize=16)
209
210     # Plot and store map
211     pyplot.scatter(x, y, c=z, cmap=cm.jet, norm=norm, zorder=2, s=
212         70, lw=0)
213     pyplot.colorbar().ax.tick_params(labels=16)
214     self.plots[stat] = outplot
215     pyplot.close()
216
217     # Generate plot of D/G ratio histogram
218     def plot_histogram(self):
219
220         # Generate histogram
221         hist,bins = numpy.histogram(numpy.array(self.mapstats["D/G"],
222             dtype=float), bins=25)
223         width = 0.7 * (bins[1] - bins[0])
224         center = (bins[:-1] + bins[1:]) / 2
225
226         # Create figure
227         outplot = pyplot.figure(figsize=(10,10))
228         pyplot.title(self.device + '_(D/G_Histogram)', fontsize=18)
229         pyplot.xlabel('D/G_(arb.)', fontsize=16)
230         pyplot.ylabel('Count_(arb.)', fontsize=16)
231         pyplot.tick_params(axis='both', which='major', labelsize=16)
232
233         pyplot.bar(center, hist, align='center', width=width)
234         self.plots['histogram'] = outplot
235         pyplot.close()
236
237     # Dot product of two spectra (0 <= dprod <= 1)
238     def dotprod(self,spec1,spec2):
239
240         dprod = numpy.dot(spec1/numpy.sum(spec1),spec2/numpy.sum(spec2)
241             )
242         return float(dprod)
243
244     # Cross-correlation coefficient (-1 <= xcorr <= 1)
245     def xcorrelate(self,spec1,spec2):

```

```

242     avg1 = numpy.average(spec1)
243     avg2 = numpy.average(spec2)
244     sqrdev1 = numpy.sum((spec1-avg1)**2)
245     sqrdev2 = numpy.sum((spec2-avg2)**2)
246     xcorr = numpy.sum((spec1-avg1)*(spec2-avg2)) / numpy.sqrt(
        sqrdev1*sqrdev2)
247     return xcorr
248
249     # Retrieve the name of the region with the highest coefficient
250     def bestregion(self, coeffs):
251         v = list(coeffs.values())
252         k = list(coeffs.keys())
253         return k[v.index(max(v))]
254
255     # Fit a peak and return the y-values in the ROI (new background
        subtraction)
256     def get_peak(self, xdata, ydata, peakname):
257
258         # Regions of interest for peaks
259         ramanroi = { 'D' : [1210.0, 1490.0], 'G' : [1470.0, 1710.0], '2
            D' : [2360.0, 2790.0] }
260         roi = [numpy.abs(xdata-ramanroi[peakname][0]).argmin(), numpy.
            abs(xdata-ramanroi[peakname][1]).argmin()]
261         xdata = xdata[roi[0]:roi[1]]
262         ydata = ydata[roi[0]:roi[1]]
263
264         # Create lmfit background parameters
265         peakparams = {}
266         peakparams['a'] = [0.0]
267         peakparams['b'] = [numpy.min(ydata)]
268
269         # Generate constraints and initial guesses for peaks
270         imax = numpy.abs(numpy.max(ydata)-ydata).argmin()
271         if peakname == 'D':
272             peakparams['center'] = [1350.0, 1335.0, 1365.0]
273             peakparams['sigma'] = [18.0, 10.5, 25.5]
274             peakparams['fraction'] = [0.7, 0.0, 1.5]
275         if peakname == 'G':
276             peakparams['center'] = [xdata[imax], xdata[imax]-5.0, xdata[
                imax]+5.0]
277             peakparams['sigma'] = [4.5, 2.0, 18.0]
278             peakparams['fraction'] = [0.7, 0.0, 1.5]

```

```

279 if peakname == '2D':
280     peakparams['center'] = [2695.0, 2680.0, 2710.0]
281     peakparams['sigma'] = [12.0, 7.0, 17.0]
282     peakparams['fraction'] = [0.7, 0.0, 1.5]
283
284 # Amplitude parameters
285 amp = (numpy.max(ydata) - numpy.min(ydata))
286 coef = [peakparams['sigma'][0]*numpy.sqrt(2*numpy.pi),
        peakparams['sigma'][2]*numpy.sqrt(2*numpy.pi)*2]
287 peakparams['amplitude'] = [coef[0]*amp, 0.0, coef[1]*amp]
288
289 # Initialize lmfit models
290 bknd = BackgroundModel()
291 peak = PseudoVoigtModel()
292 fit_model = bknd + peak
293 fit_params = fit_model.make_params()
294
295 # Set the initial fitting parameters
296 for param in peakparams.keys():
297     v = peakparams[param]
298     if len(v) == 1: fit_params[param].set(v[0])
299     else: fit_params[param].set(v[0], min=v[1], max=v[2])
300
301 # Perform fit
302 fit_out = fit_model.fit(ydata, params=fit_params, x=xdata,
        method="leastsq")
303
304 # Store background parameters
305 bknd_params = {}
306 for param_name in sorted(list(bknd._param_names)):
307     bknd_params[param_name] = fit_out.params[param_name]._val
308
309 # Store peak parameters
310 peak_params = {}
311 for param_name in sorted(list(peak._param_names)):
312     peak_params[param_name] = fit_out.params[param_name]._val
313
314 # Compute peak data array
315 pdata = numpy.array(peak.func(x=xdata, **peak_params))
316 return pdata

```


A Functions

The following defined functions were used in a number of capacities and were defined in the same library file. They are sorted into various categories.

A.2.1 Curve fitting

Custom fitting functions for use with the Lmfit Python module. Used for analyzing both MEPS and Raman data.

```
1 def pseudovoigt_model(x, amplitude=1.0, center=0.0, sigma=1.0,
2   fraction=0.7):
3     lpeak = fraction * (amplitude/(1 + ((1.0*x-center)/sigma)**2)) /
4       (numpy.pi*sigma)
5     gpeak = (1-fraction) * (amplitude/(numpy.sqrt(2*numpy.pi)*sigma)
6       ) * numpy.exp(-(1.0*x-center)**2 / (2*sigma**2))
7     return lpeak + gpeak
8
9 class PseudoVoigtModel(Model):
10     fwhm_factor = 3.60131
11     def __init__(self, *args, **kwargs):
12         super(PseudoVoigtModel, self).__init__(pseudovoigt_model, *args,
13           **kwargs)
14
15 def background_model(x, a=0.0, b=50.0):
16     return a*x + b
17
18 class BackgroundModel(Model):
19     def __init__(self, *args, **kwargs):
20         super(BackgroundModel, self).__init__(background_model, *args,
21           **kwargs)
```

A.2.2 Raman map stitching

Functions used for stitching sequential Raman maps collected for a single device.

```
1 # Shift coordinates of a Raman map
2 def shift_ramanmap(ramanmap, dx=0.0, dy=0.0):
3     tmpmap = []
4     dx dy = numpy.array([dx,dy])
5     for point in ramanmap:
6         tmpmap.append(numpy.array([point[0]+dx dy, point[1]]))
7     return numpy.array(tmpmap)
8
```

```

9 # Determine overlapping region of Raman maps
10 def calc_overlap(map0, map1, returnroi='inside'):
11     xmax = max([i[0][0] for i in map0])
12     xmin = min([i[0][0] for i in map0])
13     ymax = max([i[0][1] for i in map0])
14     ymin = min([i[0][1] for i in map0])
15     overlapmap = []
16     for point in map1:
17         if xmin <= point[0][0] < xmax and ymin <= point[0][1] < ymax
           and returnroi == 'inside':
18             overlapmap.append(point)
19         if not (xmin <= point[0][0] < xmax and ymin <= point[0][1] <
           ymax) and returnroi == 'outside':
20             overlapmap.append(point)
21     return numpy.array(overlapmap)
22
23 # Find nearest point in overlapping map
24 def findnearest(point, mapdata, dxmax=0.35, dymax=0.35):
25     vecdist = lambda u,v: numpy.sqrt((v[0]-u[0])**2 + (v[1]-u[1])**2
           )
26     maxdist = 0.55*vecdist([dxmax,dymax],[0.0,0.0])
27     distlist = numpy.array([vecdist(point[0],i[0]) for i in mapdata
           ])
28     index = distlist.argmin()
29     if min(distlist) <= maxdist: return index
30     else: return -1
31
32 # Cross-correlation coefficient (redundant with Raman class)
33 def xcorrelate(spec1,spec2):
34     avg1 = numpy.average(spec1)
35     avg2 = numpy.average(spec2)
36     sqrdev1 = numpy.sum((spec1-avg1)**2)
37     sqrdev2 = numpy.sum((spec2-avg2)**2)
38     xcorr = numpy.sum((spec1-avg1)*(spec2-avg2)) / numpy.sqrt(sqrdev
           1*sqrdev2)
39     return xcorr

```

A Code blocks

The following blocks of code exist outside the previously mentioned classes and were executed as a part of the main data analysis script as a matter of convenience.

A.3.1 Raman map stitching

This block of code performs the Raman map stitching operation. Note that an instance declared as “ramandata” was used which contains various measurement meta-data (device numbers, number of map files, paths to data, etc). Some status and diagnostic data are printed to the terminal.

```
1 print 'Importing multimap data...\n'
2 print 'Device: ',
3
4 # For map stitching
5 mapstep = 0.350
6 gridrad = 6
7 # Counter for maps stitched
8 devcount = 0
9 # Dict of devices
10 rdevices = {}
11
12 # Iterate over all devices
13 for devname in ramandata.devnames:
14
15     # Multiple map files
16     if len(ramandata.devlist[devname]) > 1:
17
18         inpath = ramandata.datapath
19         rdevices[devname] = CNTFET(device=devname)
20
21         # Load map data
22         print devname + ' ',
23         devcount += 1
24         print ' (Load: ',
25         rmaps = {}
26         for i in sorted(ramandata.devlist[devname][::-1]):
27             rmaps[i] = Raman(device=devname, filepath=inpath + devname + '
28                 /', filename=devname + '-map_' + str(i) + '.txt')
29             print i,
30             print ') ',
31
32         # Perform component analysis
33         print ' (ROI/PCA: ',
34         for mapnum in sorted(rmaps.keys()):
35             print mapnum,
36             rmaps[mapnum].load_lookup(filepath=inpath + 'region/')
```

```

36     rmaps[mapnum].classify_regions()
37     print ')\n',
38
39     # Stitch together maps
40     print '(\nStitch:\n',
41
42     # Iterate over the measured map ids from last to first
43     for n in sorted(ramandata.devlist[devname])[1:][::-1]:
44
45         print str(n)+'->'+str(n-1),
46         map0 = rmaps[n-1]
47         map1 = rmaps[n]
48         if len(map0.regionmap['cnt']) > 0 and len(map1.regionmap['cnt']
49             ]) > 0:
50             overlapmap = calc_overlap(map0.regionmap['cnt'],map1.
51                 regionmap['cnt'])
52             else:
53                 overlapmap = numpy.array([])
54
55             # Dict of maps, average shift [dx,dy], total cross-correlation
56             coeffs (float)
57             mapshift = {}
58             mapxcorr = {}
59
60             # Iterate over a grid about the map center point
61             for i in numpy.arange(-gridrad,gridrad+1,1):
62                 for j in numpy.arange(-gridrad,gridrad+1,1):
63
64                     # Keys of the dicts
65                     key = str(i)+','+str(j)
66                     shiftmap = shift_ramanmap(overlapmap, dx=i*mapstep, dy=j*
67                         mapstep)
68
69                     # Placeholder for map shifted to overlap
70                     newmap = []
71                     # Average total shift
72                     mapshift[key] = numpy.array([0.0,0.0])
73                     # Total cross-correlation coeff for whole map
74                     xcorr = 0.0
75
76                     # Iterate over points in the shifted map
77                     for point in shiftmap:

```

```

74     # Find index of nearest point
75     index = findnearest(point, map0.regionmap['cnt'])
76     if index >= 0:
77         newxy = map0.regionmap['cnt'][index][0]
78         newmap.append(numpy.array([newxy, point[1]]))
79         # Shift of the map point
80         mapshift[key] += newxy - point[0]
81         # Cross-correlate the two spectra
82         xcorr += xcorrelate(map0.regionmap['cnt'][index][1], point[
83 1])
84
85     # Avoid divide by zero
86     if len(newmap) == 0: numpoints = 1.0
87     else: numpoints = len(newmap)
88     # Average all of the map shifts
89     mapshift[key] = mapshift[key]/numpoints + numpy.array([i*
90 mapstep, j*mapstep])
91
92     # Store the total cross-correlation. No normalization favors
93     more point overlap
94     mapxcorr[key] = xcorr/numpoints
95
96 bestkey = max(mapxcorr, key=mapxcorr.get)
97
98 # Shift second map1 into position with map0
99 for i in range(0, len(map1.mapdata)):
100     newxy = map1.mapdata[i][0] + mapshift[bestkey]
101     map1.mapdata[i] = numpy.array([newxy, map1.mapdata[i][1]])
102
103 if len(map1.mapdata) > 0:
104     # Store map0 points which lie outside map1
105     uniquemap = calc_overlap(map1.mapdata, map0.mapdata,
106 returnroi='outside')
107     # Stack map1 underneath unique region of map0, store into
108     map0
109     rmaps[n-1].mapdata = numpy.vstack([uniquemap, map1.mapdata])
110 else:
111     # No CNT data, discard
112     rmaps[n-1].mapdata = map0.mapdata
113
114 print ')\n',
115 rdevices[devname].raman = rmaps[0]
116

```

```
111 | print '\nTotal␣:␣' + str(devcount)
112 | print '\n'
```

Appendix B Publications

Journal Publications

- [1] M. C. Eastman and K. S. Krane, “Neutron capture cross sections of even-mass tellurium isotopes,” *Physical Review C*, vol. 77, no. 2, p. 024303, 2008.
- [2] M. Eastman, A. Besser, Y. Chen, and J. Jiao, “Hydrothermal synthesis of Core/Shell ZnO:Mn/Mn₃O₄ nanowires,” *The Journal of Physical Chemistry C*, vol. 115, no. 22, pp. 10979–10984, 2011.
- [3] M. Eastman, D. Hedinger, W. Qian, W. Hudson, B. Jiang, and J. Jiao, “Raman spectroscopy and band structure of pd-hybridized multilayer graphene,” *Carbon*, vol. 68, pp. 687 – 694, 2014.

Conference Proceedings

- [1] M. Eastman and J. Jiao, “Electron microscopy characterization of ZnO:Mn nanowires,” *Microscopy and Microanalysis*, vol. 15, no. Supplement, 2009.
- [2] M. Eastman, H. Li, and J. Jiao, “Electron microscopy characterization of low-temperature growth zn-doped TiO₂ nanowires,” *MRS Online Proceedings Library*, vol. 1178, 2009.
- [3] M. Eastman, R. Schaller, A. Besser, and J. Jiao, “Crystalline structure and ELNES of branched Al₂O₃ nanowires,” *Microscopy and Microanalysis*, vol. 16, no. S2, p. 1788–1789, 2010.
- [4] M. Eastman, S. Fowler, P. Lommen, and J. Jiao, “Evaluation of monodisperse amorphous SiO₂/TiO₂ core-shell nanoparticles,” *Microscopy and Microanalysis*, vol. 18, no. Supplement S2, p. 1638–1639, 2012.
- [5] M. Eastman, W. Qian, D. Hedinger, A. Jacobson, B. Jiang, and J. Jiao, “Band structure and spectroscopy of graphene-pd hybrids,” *Microscopy and Microanalysis*, vol. 19, no. Supplement S2, p. 1602–1603, 2013.
- [6] M. Eastman and J. Jiao, “Coloration defects in industrial-grade zirconium sponge,” *Microscopy and Microanalysis*, vol. 21, no. S3, pp. 1779–1780, 2015.

Co-authored Publications

- [1] J. Wu, M. Eastman, T. Gutu, M. Wyse, J. Jiao, S.-M. Kim, M. Mann, Y. Zhang, and K. B. K. Teo, "Fabrication of carbon nanotube-based nanodevices using a combination technique of focused ion beam and plasma-enhanced chemical vapor deposition," *Applied Physics Letters*, vol. 91, no. 17, p. 173122, 2007.
- [2] H. Li, M. Eastman, R. Schaller, W. Hudson, and J. Jiao, "Hydrothermal synthesis of CdS nanoparticle-decorated TiO₂ nanobelts for solar cell," *Journal of Nanoscience and Nanotechnology*, vol. 11, pp. 8517–8521, Oct. 2011.
- [3] W. Qian, Z. Chen, M. Eastman, S. Cottingham, B. A. Manhat, A. M. Goforth, and J. Jiao, "Complementary microscopy techniques applied for optimizing the structure and performance of graphene-based hybrids," *Ultramicroscopy*, Nov. 2011.
- [4] C. Wang, Z. Jiang, L. Wei, Y. Chen, J. Jiao, M. Eastman, and H. Liu, "Photosensitization of TiO₂ nanorods with CdS quantum dots for photovoltaic applications: A wet-chemical approach," *Nano Energy*, vol. 1, no. 3, pp. 440 – 447, 2012.
- [5] W. Qian, R. Hao, J. Zhou, M. Eastman, B. A. Manhat, Q. Sun, A. M. Goforth, and J. Jiao, "Exfoliated graphene-supported pt and pt-based alloys as electrocatalysts for direct methanol fuel cells," *Carbon*, vol. 52, pp. 595–604, Feb. 2013.
- [6] S.-K. Chiu, B. A. Manhat, W. J. DeBenedetti, A. L. Brown, K. Fichter, T. Vu, M. Eastman, J. Jiao, and A. M. Goforth, "Aqueous red-emitting silicon nanoparticles for cellular imaging: Consequences of protecting against surface passivation by hydroxide and water for stable red emission," *Journal of Materials Research*, vol. 28, no. 02, p. 216–230, 2013.