ORGANIC ELECTRONIC DEVICES USING GRAPHENE AND HIGHLY PURIFIED THIN FILMS OF CARBON NANOTUBES AS TRANSPARENT CONDUCTIVE ELECTRODES

By

EVAN PETER DONOGHUE

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To my many teachers
ACKNOWLEDGMENTS

Writing a dissertation can be a humbling experience and as I wrote the pages that you are about to read, I was constantly reminded of how much of what I have accomplished is owed to the many friends, colleagues and teachers who have contributed both to my research efforts as well as to my own personal development. In light of the wide-ranging contributions from many different people, it seems unfair that my name stands alone on the cover of this document. I hope that they all know that I am truly appreciative of what they have given me.

First and foremost, I would like to thank my family who have helped to make me who I am and who have supported me in times of success and times of difficulty. They have always given me the love, care, encouragement and support that I have needed while allowing me to choose my own path in life. On days that I was struggling in my research or classwork, there was always a degree of comfort that came from knowing that they would be there for me. I couldn’t have made it to this point without them.

I also need to thank my advisor Andrew Rinzler for all that he’s taught me over my graduate career. From the first days, back in June 2006, I always felt that he listened to and valued my opinions and offered me his honest opinions in return. He has always been there by my side to teach me the fundamental laboratory skills that I have needed and make sure that, whatever I was doing, I was always thinking about the best way to do it – from something as simple as washing a pair of tweezers to as important as working around hazardous materials. It is hard to imagine getting a better training in hands-on experimental science. Professor Rinzler and his research were a major factor in my decision to come to the University of Florida and one of the best things I can say
about that decision is that, after six years of research, my curiosity and excitement about the future of this work has only grown with time.

My labmates have been essential to my work in this dissertation as well as my growth as a scientist. I am extremely fortunate to be surrounded by so many smart, driven and fun people who have helped me in my research and kept me sane in the process and for that I thank Bo Liu, Mitchell McCarthy, Pooja Wadhwa, Rajib Das, Maureen Petterson, Max Lemaitre, Svetlana Vasilyeva, Xiao Chen, Yu Shen, Ramesh Jayaraman, Matt Gilbert, Tom Hayman, Stephen French, Kyle Dorsey, and Zhuangchun Wu. I cannot count how many problems I have overcome simply by talking to my colleagues or how often they have been willing to contribute their time and effort to advancing my work. I want to particularly thank Bo Liu for helping me when I needed him most, offering me ideas for projects to undertake and keeping me calm with his even-keeled support and encouragement. I also need to single out Mitchell McCarthy’s effort (in conjunction with Bill Malphurs of the Machine Shop) in designing the glovebox and evaporators that have enabled so much of the work in our lab. Ramesh Jayaraman (in addition to Maureen Petterson and others) has played an often underappreciated role in carbon nanotube synthesis to provide the material that drives all of the research in our lab and I owe him my thanks. Similarly, Max Lemaitre and I worked side-by-side on the efforts in G-VFETs for Chapter 4 and the work there was shared – though he also grew all the graphene himself and brought the idea of the improved transfer technique.

I also need to thank all of our collaborators, starting with Prof John Reynolds and his group in the Department of Chemistry (now at Georgia Tech). Professor Reynolds
was always a calming presence who kept an eye on the big picture and on many occasions was there with an encouraging word and a suggestion for future work. He always seemed to be looking out for me and I am truly grateful for his role in my research. I was also fortunate to meet his student, Ken Graham, early in my career so that I could develop and learn alongside him on projects such as the organic light emitting diode work of Chapter Five. I’ve enjoyed having him as a friend and colleague and I hope that can continue into the future. There are many others who I worked alongside in MCCL and the Chemistry Department that have helped me along this journey, namely Nathan Heston, Aubrey Dyer, Ryan Walczak, Egle Puodziukynaite, Richard Farley, Caroline Grand, Patrick Wieruszewski, Justin Oberst and Danielle Salazar and I would like to thank all of them.

Similarly, Professor Art Hebard’s group has always had a strong relationship with our laboratory and we have relied on each other for both equipment and insight. I want to particularly thank Patrick Mickel, Sefaattin Tongay, and Kara Berke. Additionally, Dr. Franky So and his group have assisted ours in many ways and I am appreciative of their contributions.

During my first visit to the University of Florida, as Professor Hebard showed me around the building he made a point of raving about the excellence of the support staff in the Physics Department. At the time, this statement did not mean much to me but after six years, I cannot fathom what the department would do without them. So much of the equipment in our lab has been built by Ed Storch, Bill Malphurs and Marc Link that to remove their contributions would be to eliminate 75% of the results found in this document. Similarly, I could always count on Jay Horton to help in any way he could
whether that was maintaining pumps or installing fume hoods. Greg Labbe and John Graham in Cryogenics, everyone in the Electronics Shop, the custodial staff and Tim Noland have always been there to keep our experiments and our lab running smoothly. Along the same lines, Darlene Lattimer is the unsung hero of our laboratory and has kept things going behind the scenes and never once complained (to me at least) about having to save me from my own mistakes in purchasing. I also need to thank Nathan Williams and Pam Marlin for keeping me on track and never getting upset over my often late paperwork.

It was important to me that I assemble an advisory committee of people that I respected, admired and enjoyed being around. When I was deciding between graduate schools, one of the factors that drew me to Florida was the passion for science that I could immediately sense in meetings with Prof Tanner and Prof Hebard and it was this same passion for science that led to me asking them to serve on my committee. It is clear that they love their work and love to learn and I hope that I can always maintain the same excitement in my work. I’ve been fortunate to get to know Professor Tanner as his student in Optical Effects in Solids as well as a collaborator in multiple research projects in electrochromics. I’ve already mentioned the importance of the collaboration between Professor Hebard’s research group and our laboratory and I appreciate his insight and brief chats in the hall. I first got to know Professor Monkhorst in taking Solid State Physics where his excitement for the material and physics in general was always conveyed in discussions. When I see him, he seems to have a sense for when I’m down and I have always appreciated his encouragement and motivation and I’m glad to have him on my committee. Prof Kirk Ziegler has a shared interest in carbon nanotubes
and has supported my research by loaning our laboratory both equipment and materials so that we could test new ideas and I am thankful for his contributions. I am truly appreciative of all the time and energy that my committee has put into helping me become a better scientist and in helping me through this process.

I am indebted to my many friends throughout my life who have pushed me, supported me and driven me to be better. I have had many friends to lean on here in Gainesville but I’d like to thank Maureen Petterson, Denise Bloom, Pat Mickel, Joe Gartner, and Ronny Remmington for helping make my time in Gainesville more enjoyable. And I want to single out, above all, Kyle Thompson who has been my roommate for the past 6 years. More than anyone else, he has always been there for me to understand what I was going through and listen patiently when needed. There is no way that I can fully express my gratitude. I don’t know if I could have made it through graduate school without him.

Finally, I’d like to thank my many teachers – not just here at the University of Florida but through my life. Thinking back to all the little things that I’ve learned in school, from first gripping a pencil to learning my multiplication tables, there have been so many educators who have each played a key role in my journey towards a PhD. At the time they knew me my future in life was (and still is unknown) but they each imparted so many little pieces of knowledge that have summed together to help me achieve this PhD. I will never be able to thank them all but they have each made a contribution, big or small, to my progression to this point and the continuation of the journey onwards. As a token of my appreciation, I dedicate this dissertation to them.
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<td>AFM</td>
<td>Atomic force microscope</td>
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<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
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<tr>
<td>BCB</td>
<td>Benzocyclobutene</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal-oxide-semiconductor</td>
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<tr>
<td>CN-VFET</td>
<td>Carbon nanotube-enable vertical field effect transistor</td>
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<td>CVD</td>
<td>Chemical vapor deposition</td>
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<td>DNTT</td>
<td>Dinaphtho-[2,3-b:2',3'-f]thieno[3,2-b]-thiophene</td>
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<tr>
<td>DOS</td>
<td>Density of electronic states</td>
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<td>DPLV</td>
<td>Dual pulsed laser vaporization</td>
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<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
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<td>FE</td>
<td>Field effect</td>
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<tr>
<td>FET</td>
<td>Field effect transistor</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>ITO</td>
<td>Tin-doped indium oxide</td>
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<tr>
<td>LEC</td>
<td>Light emitting electrochemical cell</td>
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<tr>
<td>LiOTf</td>
<td>Lithium triflate</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<tr>
<td>MCE</td>
<td>Mixed cellulose ester</td>
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<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene]</td>
</tr>
<tr>
<td>MoOx</td>
<td>Molybdenum oxide</td>
</tr>
<tr>
<td>Mw</td>
<td>Molecular weight</td>
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<tr>
<td>NPD</td>
<td>N,N'-di(1-naphthyl)-N,N'-diphenyl-1,1'-diphenyl-1,4'-diamine</td>
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<td>OLED</td>
<td>Organic light emitting diode</td>
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<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
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<tr>
<td>Acronym</td>
<td>Full Form</td>
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<tr>
<td>PAA</td>
<td>Poly(acrylic acid)</td>
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<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
</tr>
<tr>
<td>PLV</td>
<td>Pulsed laser vaporization</td>
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<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate</td>
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<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
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<tr>
<td>SCL</td>
<td>Space charge limited</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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<tr>
<td>SWNT</td>
<td>Single walled carbon nanotube</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
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<tr>
<td>TFT</td>
<td>Thin film transistor</td>
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<td>VFET</td>
<td>Vertical field effect transistor</td>
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The impressive electrical, optical and mechanical properties of thin films of single walled carbon nanotubes (SWNTs) and graphene have sparked intense interest and extensive research into these materials, with significant recent efforts seeking to incorporate them into organic electronic devices. Generally, this work has not taken full advantage of the unique properties of these materials, such as a low density of electronic states, mechanical flexibility and an enhanced surface area for charge injection. Progress has been further stymied by particulates in the SWNT material that creates vertical protrusions into the thin organic active layer.

This dissertation will discuss applications in which the unique properties of these materials can be tested or exploited in practical organic electronic devices. The low density of electronic states found in SWNTs and graphene allows for modulation of their Fermi level, providing a new degree of freedom for tuning electronic transport that was recently demonstrated in carbon nanotube-enabled vertical field effect transistors (CN-VFETs). Thin films of SWNTs or graphene were used to probe this Schottky barrier height and width modulation and demonstrate the first graphene-enabled VFET, as well
as demonstrating solution processable and \( n \)-type CN-VFETs. Additionally, thin films of SWNTs were incorporated into organic light emitting diodes and organic light emitting electrochemical cells to study whether the properties of the carbon nanotube films offer any intrinsic advantages over more conventional electrodes. The mechanical flexibility of the SWNT film also makes possible a new dual emissive device structure in which a light emitting electrochemical cell that incorporates transparent SWNT films as both anode and cathode to emit light in both the forward and reverse direction.

In addition to this device-based work, extensive research into carbon nanotube purification techniques will be discussed including the adaptation of a scalable purification technique not previously demonstrated with materials on this length scale. Material made available by this large-scale purification technique were incorporated into CN-VFETs that use the thinnest organic channels ever achieved in these devices. These projects offer insights into the special role that SWNTs can play in organic electronic devices.
CHAPTER 1
INTRODUCTION AND BACKGROUND

Physical and Electronic Structure of Graphene

The two-dimensional honeycomb carbon lattice of graphene offers a material system that couples near ballistic charge transport (with mobilities exceeding 200,000 cm\(^2/V\cdot s\))\(^1\) across a planar material with high optical transparency. Though graphene has been the subject of theoretical inquiry for over sixty years\(^2\)\(^-\)\(^4\), it was not considered to occur as physically stable structure until 2004 when it was accessed experimentally for the first time through the mechanical exfoliation of graphene from graphite\(^5\)\(^,\)\(^6\). Since this initial realization, graphene synthesis has been demonstrated using a range of methods beyond mechanical exfoliation such as epitaxial growth\(^7\)\(^-\)\(^9\), chemical vapor deposition (CVD)\(^10\)\(^,\)\(^11\) and reduction from graphite oxide flakes\(^12\)\(^,\)\(^13\). These techniques, and others, have allowed for the creation of large area films of graphene\(^11\)\(^,\)\(^14\)\(^,\)\(^15\) and wide ranging studies into its fundamental physical properties\(^16\)\(^-\)\(^19\).

Graphene’s honeycomb lattice of sp\(^2\) bonded carbon is the source of many of its interesting electrical properties that we seek to take advantage of in this dissertation. The symmetry in graphene’s physical structure allows us to approximate its electronic structure using an orthogonal nearest-neighbor tight-binding model where its electronic states can be approximated by a linear combination of 2p\(_z\) orbitals\(^19\). Solving using the Schrödinger equation yields the dispersion relations for the bonding (\(\pi\)) and anti-bonding (\(\pi^*\)) bands as:

\[
E(k_x,k_y) = \pm \gamma \sqrt{1 + 4 \cos \left( \frac{\sqrt{3}k_xa}{2} \right) \cos \left( \frac{k_ya}{2} \right) + 4 \left[ \cos \left( \frac{k_ya}{2} \right) \right]^2}
\]

(Eq. 1-1)
where \( k_x \) and \( k_y \) define the components of the \( k \) vector in the first Brillouin zone and \( \gamma \) is the nearest neighbor hoping integral (2.75 eV). This results in symmetric conduction and valence bands, with respect to the Fermi energy, that meet at six \( K \) and \( K' \) points also known as the Dirac points. The density of states is zero at the Dirac point and increases linearly as energy increases away from the Fermi energy\textsuperscript{20}. This low density of states will be exploited in the Chapter 3 discussion of vertical field effect transistors where we will use graphene to disentangle the operational mechanisms of this new device architecture.

**Physical and Electronic Structure of Single Walled Carbon Nanotubes**

An individual single walled carbon nanotube (SWNT) can be conceptually visualized as a single graphene lattice rolled into a seamless cylindrical tube that can be microns to millimeters in length and between 0.6 nm and 10 nm in diameter. The wrapping of this tube perpendicular to the tube axis is defined by the chiral vector, \( C_h \), which itself is composed of two non-orthogonal vectors \( a_1 \) and \( a_2 \) that access each site of the graphene sheet (Figure 1-1)\textsuperscript{21, 22}. The chiral vector, \( C_h \), is defined as:

\[
C_h = n \; a_1 + m \; a_2 \; (n,m \text{ are integers with } 0 \leq |m| \leq n)
\]

(Eq. 1-2)

which is more commonly abbreviated by its vector indices \((n,m)\) to define the structure, or chirality, of any given SWNT. The physical structure of the SWNTs allows us to consider them a quasi-1D material offering near ballistic on-tube transport that remains defect tolerant.

While a single graphene sheet is considered a zero gap semiconductor, the confinement along \( C_h \) introduced in SWNTs has a significant impact on the electronic structure by imparting periodic boundary conditions in the circumferential direction and quantizing the wave vector along the chiral vector, while the wave vector along the axis
of the nanotube remains continuous. The 1D energy dispersion relationships of SWNTs are effectively cross-sectional cuts of the 2D graphene energy dispersion relation. If this cut crosses one of the six $K$ points where the $\pi$ and $\pi^*$ bands touch in the first Brillouin zone of graphene, the nanotube will also have zero bandgap making it metallic. However, if this cut avoids the $K$ point, there will be a nonzero band gap and the nanotube will be semiconducting.

This relation can also be calculated by applying the aforementioned periodic boundary conditions to the wave vector and solving for the energy relations in the Schrödinger equation to yield the electronic density of states as shown for a demonstrative metallic and semiconducting SWNT in Figure 1. A non-zero density of states at the Fermi energy ($E=0$), renders one-third of all carbon nanotubes metallic while the remaining two-thirds possess a finite energy gap between the valence and conduction bands and are semiconducting. This relationship can be formalized and the type of any given nanotube can be determined from the vector indices where any tube for which $(n-m)/3$ is equal to an integer will act as a metal and all others will act as a semiconductor.

The reduced dimensionality of SWNTs leads to a very low density of states near the Fermi level in all carbon nanotubes. As a result, the Fermi level of a SWNT can be widely modulated through charge transfer chemical doping as well as through gating by an external field. The implications of these Fermi levels shifts will be discussed in Chapter 3 where tuning of the Schottky barrier at the SWNT / organic semiconductor will admit device mechanisms not available for higher DOS conventional metals.
Figure 1-1. Schematic indicating graphene lattice with $a_1$, $a_2$ and the chiral vector, $C_h$, as shown. Parallel dashed lines indicate nanotube axis. In this example, a (5,3) tube is demonstrated. Reprinted with permission from Dresselhaus et al.31.

Figure 1-2. Electronic density of states of A) a (10,0) nanotube and B) a (9,0) nanotube. Reprinted with permission from Saito et al.21.

**Transparent Conductive Thin Films of Single Walled Carbon Nanotubes**

While individual SWNTs have demonstrated impressive characteristics and have been utilized to demonstrate a range of devices27,32-37, separation and manipulation of individual SWNTs is challenging and can be difficult to incorporate into practical devices. However, by assembling these SWNT into a thin film, they can act as the transparent conductive electrodes required for many organic electronic device technologies (Figure 1-3). In the eight years since their introduction by Wu et al.38, thin films of SWNTs have been incorporated into numerous devices across a range of
applications\textsuperscript{29, 30, 39-47} – some of which will be discussed in greater detail in this dissertation.

![Image](image_url)

Figure 1-3. A) Thin film of single walled carbon nanotubes taken by a scanning electron microscope. B) Transmittance of ITO and SWNT films of varying thicknesses. C) Diagram of various application enabled by thin films of SWNTs in the Rinzler laboratory.

Though thin films of SWNTs preserve many of the properties of individual SWNTs, there are a few distinctions worth noting. Individual carbon nanotubes have been shown to be near ballistic conductors with intrinsic carrier mobilities in an individual semiconducting tube on the order of 100,000 cm\(^2\)/V\(-\)s, among the highest values reported in a semiconducting material\textsuperscript{48}, however, when a nanotube network is formed, the conductance is dominated by the impedance to charge transport across tube-tube junctions\textsuperscript{49}. While the resistance along an individual SWNT is on the order of tens of kΩs (approaching the 6kΩ limit predicted for length independent ballistic transport)\textsuperscript{33, 50, 51}, the resistance at a crossed metal-metal or semiconducting-semiconducting SWNT junction was found to be approximately 200 kΩ while a metal-semiconducting SWNT
junction was several orders of magnitude worse due to the presence of a Schotky barrier. Thus, to first order, the conductivity of thin film networks of SWNTs is heavily dependent on average tube length, as longer tubes require fewer tube-tube junctions, with the network conductivity ($\sigma_{DC}$) proportional to average tube length ($L$) to the 1.46 power ($\sigma_{DC} \sim L_{avg}^{1.46}$). Likewise, the sheet resistance is inversely proportional to film thickness as thicker films offer a greater probability of the more conductive pathways across similar nanotube junctions. This relation goes as $R_s = \frac{1}{\sigma_{DC}t}$ where $t$ is the film thickness and $\sigma_{DC}$, the dc conductivity, is strongly dependent upon on factors such as the connectivity of nanotube-nanotube junctions, doping, and tube length which will vary widely with preparation technique.

While clearly the impedance at SWNT-SWNT junction plays a major role in thin films of SWNTs, the conductivity loss should not be overstated. Highly conductive and transparent films of single walled carbon nanotubes have been produced, with conductivities as high as 6600 S/cm$^2$ and sheet resistances as low as 30 $\Omega/\square$ for 50 nm thick films that are 70% transparent through the visible spectra. This level of performance is below that of conventional transparent conductive oxides, such as tin-doped indium oxide (ITO) which at 90% transparency can posses sheet resistances approaching 10 $\Omega/\square$, but remains high enough for incorporation as an ITO replacement in some applications where their similar work functions (4.6-4.9 eV for SWNTs vs. 4.4 – 4.9 eV for ITO) make SWNT films a promising alternative.

In other devices, the SWNT film can offer benefits and access modes of operation that are not achievable by ITO or conventional metals. For example, unlike conventional electrodes which offer only a planar surface for charge injection, the 3D
structure and porosity offered by a SWNT film offers an enhanced surface area, particularly when used with solution processable active layers that can penetrate into the porous SWNT network and access charge injection from all sides of a SWNT. In a 50 nm thick film, where the inter-SWNT porosity is on the order of the length scale of the SWNTs themselves, it was estimated via double layer capacitance measurements that the surface area was 2.5 times greater than a planar palladium electrode. Other advantages of SWNT films over conventional metals include their mechanical flexibility, room temperature and pressure film fabrication, and low density of electronic states allowing for Fermi level shifting (expanded upon in Chapter 3).

Fabrication of these thin films of SWNTs can be achieved through a variety of methods though one of the most common techniques is through vacuum filtration as described by Wu et al. Purified SWNTs (growth and purification of SWNTs will be covered in Chapter 2) are suspended in a surfactant solution which is subsequently vacuum filtered in a dead ended filtration through a porous, mixed cellulose ester (MCE) membrane, trapping the SWNTs on the surface of the membrane as the liquid is sucked through the membrane. After allowing the membrane to dry, washing with deionized water removes the surfactant shell coating the SWNTs. These films can be adhered to the surface of a substrate through heat and pressure, with the evaporation of a small amount of water or isopropanol helping to pull the film into more intimate contact and forming van der Waals bonds between the SWNT film and the substrate. An acetone vapor bath gently dissolves the MCE membrane, leaving a pristine SWNT film adhered to the substrate and ready for device preparation. This technique has enabled SWNT films transferred to materials including glass, silicon, sapphire, quartz, Teflon,
poly(ethylene) and poly(ethylene terephthalate) and offers facile control over film thickness / density simply through manipulation of the concentration and volume of SWNT solution that is filtered. These films will form the foundation of much of the work explored in this dissertation.

**Organic Semiconductors**

Though the semiconductor electronics industry has been dominated by research into inorganic materials such as silicon or III-V semiconductors, developments in organic semiconductors over recent decades has revealed the important role that these materials can play in practical devices. The ability to widely tune the optoelectronic properties of organic semiconductors through synthetic structural modification enables their incorporation into an array of organic electronic devices that span a similarly wide range of device properties and functions. While inorganic materials have typically demonstrated higher levels of performance, organic semiconductors and the organic electronic devices that they make possible offer advantages in their potential for low energy, inexpensive manufacture with a high throughput for flexible and lightweight devices that may offset the performance gap by enabling affordable, widespread electronics.

Organic semiconductors are $\pi$-conjugated carbon-based materials that can either be small molecules (typically deposited through thermally evaporation) or polymers with repeated structural units which are traditionally dissolved in solution and deposited through techniques such as spin coating, ink-jet printing or spray casting. These materials derive their conductive properties from the delocalization of their $\pi$-electrons across the molecular chain, enabling long range electronic mobility. Materials are often
characterized by their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) which develops into a band-like structure as the number of energetic states increases, analogous to the valence and conduction band, respectively, of inorganic materials.

Charge transport within organic semiconducting layers is controlled by two processes: intramolecular mobility and intermolecular transport. Though mobilities within individual organic semiconductors molecules can be quite large, because the organic semiconducting layers are composed discrete molecular units held together only by relatively weak van der Waals bonds, the mobilities of these materials in bulk are orders of magnitude below their inorganic counterparts. Transport across molecules occurs via a hopping of free carriers from molecule to molecule, a process that is heavily influenced by factors such as the crystallinity, energetic disorder, conjugation length and charge traps present in these materials as well as the direction of charge transport as many of these materials can have large anisotropies in their mobilities. As will be seen throughout this dissertation, the low mobilities of organic semiconductors affects the performance of electronic devices by restricting organic layers to be just a few hundred nanometers thick – motivating the purification work of Chapter Two as well as the novel vertical field effect transistor of Chapters Three and Four.
CHAPTER 2
PURIFICATION OF SINGLE WALLED CARBON NANOTUBES

Overview

The use of single walled carbon nanotubes (SWNTs) in both organic electronic devices and general studies is largely reliant on access to pristine carbon nanotubes. As the bulk growth of SWNTs generates amorphous carbon, fullerenes and other carbonaceous structures in addition to residual metallic catalyst particles\textsuperscript{60-62}, careful purification of the SWNT growth product is required. The importance of this purification is especially relevant in organic electronic devices where the relatively low mobility of organic materials limits organic layers to the order of a few hundred nanometers or thinner. The presence of particulates in the SWNT electrode can create shorting pathways that extend through the organic layer, severely limiting device performance. On a laboratory scale these issues have been overcome through the use of thick organic active layers\textsuperscript{43} or a highly doped, conductive hole transport / planarizing layer\textsuperscript{41,63} but, while such workarounds allow devices to function at reasonable levels, performance still remains below what can be achieved in devices with thinner organic layers. Fabrication is simplified and material usage reduced if these layers can be eliminated.

The purification of carbon nanotubes has progressed significantly since early efforts focusing on oxidative means\textsuperscript{64-71} or low speed centrifugation\textsuperscript{72,73}. Density gradient centrifugation has recently enabled impressive advances allowing selection by electronic type, band-gap, diameter or even chirality\textsuperscript{74-76}. While this level of control is indeed impressive, it relies on separation of the bundled SWNTs by prolonged ultrasonication\textsuperscript{37}. Sonochemistry done by high energy cavitation bubbles during this
process can introduce defect sites into the SWNT sidewall and even cut the nanotubes\textsuperscript{71,77-79} to significantly shorter lengths. As a result, this technique tends to yield lower conductivity materials that are not ideal for use as transparent conductive electrodes. Further, the scalability of such a technique has not been studied and is currently limited by what can be accommodated by the centrifuge rotor and vials (though schemes to overcome this have been suggested\textsuperscript{74,80}). While batch processing can provide enough material to accommodate present laboratory needs, real world manufacturing is likely to require a significantly higher throughput.

In this chapter, I will give a brief overview of SWNT growth as it pertains to purification and review the conventional purification techniques that I have carried out in the Rinzler Laboratory. After discussing the sources of shorts found in films made from this material after standard purifications, I will present several approaches, some novel and some adapted from known literature, towards further purification of the nanotubes and discuss how I have implemented these procedures to eliminate shorting pathways. Most notably, I will introduce the first demonstration of the use of a continuous flow centrifuge to purify materials of a SWNT-length scale and show how the extremely high levels of purity achieved through this method has enabled organic active layers as thin as 100 nm in this readily scalable technique.

**Single Walled Carbon Nanotube Synthesis by Dual Pulsed Laser Vaporization**

Sumio Iijima discovered carbon nanotubes in 1991 as the residual by-product remaining on the cathode of his arc reactor during fullerene growth\textsuperscript{81}. In the ensuing years, much effort was focused on the development of a means of synthesizing high quality, defect-free SWNTs at low cost for the studies and potential applications that require their use. Numerous growth methods and techniques have been developed in
this pursuit, most notably arc discharge\textsuperscript{82, 83}, chemical vapor deposition (CVD)\textsuperscript{84, 85}, and pulsed laser vaporization (PLV)\textsuperscript{61, 86, 87}. Though each technique has its own merits and disadvantages, PLV-grown SWNTs are typically considered to have the lowest defect density while maintaining long tube-length, rendering the high conductivity material desired for organic electronic devices. As such, all studies discussed in this dissertation use PLV-grown SWNTs synthesized either in the Smalley Laboratory at Rice University or using an in-house built and operated system within the Rinzler Laboratory at the University of Florida. Though synthesis of carbon nanotubes was carried out by colleagues and is not part of this dissertation, the growth of high quality SWNTs is an essential part of all experiments and as such, it will be briefly summarized here.

In this technique (also known as dual pulsed laser vaporization, or DPLV), two high powered laser pulses strike a carbon target (98 wt % carbon, 1 wt % each Co and Ni) in a quartz tube furnace at high temperature (1150 - 1200°C) under a partial argon environment (500 mTorr). The first pulse is at 532 nm (15 W) to preheat the target followed by a second pulse 39 ns later, after the heat pulse has penetrated into the target, at 1064 nm (25 W) to locally vaporize the target and form a plume of ablated carbonaceous precursors composed of monoatomic carbon as well as its dimers, trimers and longer chains that is confined by a smaller diameter inner tube. The plume lasts just microseconds and in the absence of metal catalyst particles these structures would rapidly close and form self-satisfied fullerenes; however, in the presence of \textasciitilde{}1% catalyst material, SWNTs are formed.\textsuperscript{61} In this manner, high quality SWNTs can be grown at a rate of a few hundred mg/hr and collected as a wispy, tumbleweed-like soot at the end of each run.
Conventional Purification of Carbon Nanotubes in the Rinzler Laboratory

The SWNTs in the PLV-grown soot has by-products including metal catalyst particles, amorphous carbon, fullerenes and spheroidal “bucky onions” which are self-satisfied carbon shells with a diameter of 1-5 nm that can either be hollow or can have a metal catalyst core. These assorted contaminants intrinsic to the growth process must be eliminated for most applications and there are a variety of techniques used and studied – indeed a few novel techniques will be explored here. In this section I will introduce typical techniques used in the Rinzler laboratory, that constitute refinements of methods developed by Rinzler et al. in the Smalley Laboratory, before examining additional techniques explored in my work.

Nitric Acid Reflux

The PLV-grown, SWNT soot (Figure 2-1) is dispersed in 1.6 M nitric acid which then undergoes a 45 hour nitric acid reflux in which the solution is boiled in a round bottom flask with a condenser returning evaporated liquids back to the solution (Figure 2-2). During this process, the nitric acid readily attacks and dissolves any loose metallic catalyst particles spalled during the growth as well as any amorphous carbons which are dissolved as humic acids. While most carbon structures containing self-satisfied carbon bonds (such as fullerenes, bucky onions or the pristine SWNT sidewall) are not attacked, any dangling bonds and even the nanotube end-cap, which is less stable than the nanotube sidewall, can be attacked and gradually eaten away followed by the gradual destruction of the nanotube from the end. Similarly, defect sites on the carbon nanotube sidewall offer dangling bonds that permit dissolution by nitric acid and can cut the carbon nanotubes into pieces. All this has the detrimental effect of substantially lowering the post-reflux SWNT yield but with the benefit that only the long, pristine,
defect-free SWNTs remain; yielding a final product that may have better electrical properties than would be achieved if these lower quality tubes were not destroyed.

The nitric acid reflux has an added benefit beyond dissolution of the various DPLV by-products; it also serves to substantially dope the SWNTs p-type. This doping helps give high conductivities to the semiconducting SWNTs, rendering them near metallic in their behavior (and indeed, we shall treat them largely as such here). The SWNT doping achieved here is a relatively stable process and remains essentially unchanged even after years in solution.

After 45 hours of refluxing in nitric acid, the SWNTs are removed from the 1.6 M acid solution by repeated dilution (with deionized water) and centrifugation/decantation steps in which the nanotubes settle as sediment. This process is repeated until the solution reaches pH 4-5 at which point the nanotubes are suspended in a slightly basic surfactant solution (1% Triton-X-100 with dissolved NaOH to achieve pH 10 or 11). At this stage, many of the associated growth products have been broken down but remain in solution either as humic acid or partially dissolved solids.

**Cross Flow Filtration**

Following the nitric acid reflux, some of the dissolved by-products have been removed during the dilution and centrifugation steps; however, it becomes necessary to remove the remaining fraction in addition to the assorted self-satisfied carbon structures such as fullerenes and bucky onions that are not desired in the final product. This is partially achieved through a cross-flow filtration in which the nanotube solution is cycled through a hollow-fiber filter with 200 nm pores. The nanotubes, microns in length, cannot permeate through these pores and remain trapped within the hollow fibers while
Figure 2-1. DPLV grown SWNTs in flask immediately prior to nitric acid reflux.

Figure 2-2. Nitric acid reflux in progress in the clean room fume hood. The SWNTs are dispersed in 2.6 M nitric acid in a round bottom flask which is submerged in a hot oil bath maintaining the temperature at 230°C. Chilled water is flowed the cylindrical condenser on top to prevent escape of gaseous nitric acid.
Figure 2-3. Crossflow filtration assembly. The peristaltic pump is enclosed by a large box and connected to a fan to remove particulates before they can escape to the clean room environment.

Figure 2-4. Samplings of the eliminated supernatant during crossflow filtration with every sample representing an additional hour of crossflow filtration. Far left is sampled 1 hour after beginning crossflow filtration. Far right is sampled after 22 hours of filtration.
the dissolved by-products and structures smaller than 200 nm are flushed out and replaced with fresh surfactant solution (Figure 2-3). Periodic reversals of the flow prevent the SWNTs from accumulating on the inside of the hollow fibers and clogging the pores. Similarly, brief sonication once an hour prevents the SWNTs from excessive bundling which might clog the fibers. The cross-flow filtration is run until the permeate runs clear (Figure 2-4), indicating that the majority of the dissolved by-products and structures smaller than 200 nm have been removed. This process can take over 60 hours to complete and involve flushing more than 75 L of pure surfactant buffer solution.

At this stage, having dissolved and eliminated amorphous carbons and removed particulates smaller than 200 nm, the material can go in a variety of directions for future steps to eliminate contaminants that did not fit through the 200 nm pore size of the hollow fiber filter. The traditional processes within the Rinzler Laboratory have involved a 6000 RPM centrifugation of the concentrated nanotube solution to remove many of the larger particulates as sediment and then a dead-ended filtration of a diluted fraction of the solution through 650 nm pores. At this stage, having eliminated particles greater than 650 nm and smaller than 200 nm, the solution is used to make films for general use; however, the remaining particles in the 200 nm – 650 nm range remain highly problematic for the performance of thin organic devices. Because we are searching for a universal means of eliminating particulates, these final two steps (low speed centrifugation and 650 nm filtration) are not incorporated into the purification processes discussed below.

**Shorting Pathways from SWNT Thin Films through Organic Layers**

Shorting occurs in SWNT/organic devices when the conductive SWNT thin film extends upwards and protrudes through a relatively thin (100 – 500 nm) organic layer
deposited on top of the SWNT film (Figure 2-5A). These protrusions can arise from a range of issues – some intrinsic to SWNT growth and others from sample handling. A common problem is particulates on the surface of the substrate, which can come from an array of sources such as shards generated from dicing the substrate or airborne particulates landing on the sample. Though these particles themselves may not be conductive, a SWNT film transferred on top of the particle makes this protrusion of the film a potential electrical short (Figure 2-5B). These problems can largely be overcome through proper handling and cleaning. To this end, one early project was a comparison of different cleaning techniques on glass, with characterization by atomic force microscopy (AFM) to assay efficacy. It was determined that dicing glass under soapy water (alconox) followed by scrubbing with an ultrasonic toothbrush was more effective than simple ultrasonication in cleaning substrates. Through the adoption of this cleaning technique in addition to the development of other methods and appropriate sample preparation in a cleanroom environment, shorting from external particulates can largely be avoided.

Another source of shorting that was discovered in early SWNT films arose from defects and scratches that existed on the surface of the mixed cellulose ester (MCE) membrane, likely introduced during the membrane manufacturing process. SWNTs could accumulate or deposit in these scratches and when the SWNT film was transferred to a substrate, the accumulated SWNTs would create ridges and folds in the nanotube film (Figure 2-5C). These features could extend through the organic active layer. To avoid this problem, membranes were ordered and tested from 5 different
manufacturers and it was determined that Sterlitech membranes largely avoided the scratches seen in membranes from other manufacturers.

These are two examples of shorting pathways arising from extrinsic issues which are avoidable with appropriate care and handling. Much more prevalent and difficult to remove are the growth products intrinsic to the synthesis of SWNTs. Though exposed metal catalyst particles and amorphous carbons are dissolved during the nitric acid reflux, there are many other carbonaceous structures that have self-satisfied carbon bonds. These materials are so difficult to remove because they are structurally and chemically similar to the SWNTs and can possess a similar density. Most techniques that would chemically target these structures would likely also simultaneously attack the SWNTs.

Figure 2-6 shows high resolution transmission electron microscope (TEM) images of ‘bucky onions,’ the name for carbon shells, which here are formed around metal cores that were revealed by energy dispersive spectroscopy (EDS) to be the cobalt and nickel catalysts from SWNT synthesis. Individually, these bucky onions are small (~5 nm) and should be flushed out during the cross-flow filtration but we observed that they frequently cluster together, forming extended structures that can be several hundred nanometers in size and do not seem to break-up with moderate sonication. It was found that the major fraction of the particulates were composed of aggregates of these bucky onions, both hollow and with a metal catalyst core. Sampling by EDS found very few external contaminants present in the sample, that is to say very few particles composed of elements other than carbon, cobalt or nickel, which indicates that these particulates are indeed being generated during the SWNT synthesis.
Extensive TEM, done over wide regions of the nanotube film, indicates that these bucky onion agglomerates are the predominant particulate that remains after a nitric acid reflux and cross-flow filtration. Atomic force microscope images reveal how problematic these can be (Figure 2-7A & B) in thin SWNT films. A secondary nitric acid reflux and cross-flow filtration was tested to break-up and filter out these agglomerates with some initial success (Figure 2-7C & D); however, it did not appear that we would be able to fully eliminate these bucky onion clusters using such means. Further, the secondary nitric acid reflux did increase the sheet resistance of these films by 10 – 20% so it seems that additional nitric acid refluxes will further damage the SWNTs, consistent with reports that nitric acid refluxes of already purified material attacks the SWNTs more aggressively than in an initial reflux where the oxidation debris products actually protect the SWNTs from damage\textsuperscript{88}. The remainder of this chapter will explore methods to overcome and avoid these particulates intrinsic to the SWNT suspension.

Figure 2-5. A) AFM image of SWNT film ridge protruding through organic material with shadowed region behind ridge, B) SEM image of particle trapped under SWNT film, C) AFM image of ridge in SWNT film caused by scratches in MCE membrane.
Figure 2-6. Characteristic TEM images of aggregated bucky onions and metallic catalyst particles which are indicated by the dark, high contrast regions. The scale varies across the images as indicated. In many images, particularly at high magnification, the graphitic walls of the bucky onions and SWNTs can be resolved.
Figure 2-7. A) Height and B) amplitude AFM image of film fabricated from PLV grown SWNTs after undergoing a 45 hour nitric acid reflux (2.6 M) and 27 hours of crossflow filtration. C) Height and D) amplitude image after secondary nitric acid reflux (21 hours, 66 hours total) and secondary crossflow filtration (11 hours, 61 hours total). Full height scale in each image is 300nm.

Conformal Layers to Achieve Flat Films

Though this chapter largely discusses purification in the sense of eliminating particulates, one early effort focused on overcoming rather than removing these particles by accessing the ‘back’ side of the film. When the film is transferred, it is brought into intimate contact with the substrate and, while particulates or defects may cause protrusions on the side away from the substrate, the side of the film in contact with the substrate is forced to be as flat as the substrate itself. It is this side of the film that we attempted to access.
To access this side of the SWNT film, a thin (~1 μm) water soluble layer was spuncast onto a glass substrate to create a ‘sacrificial’ layer that is flatter than the initial glass itself (root mean square roughness is 0.16 nm vs. 0.21 nm for glass); here, poly(acrylic acid) (PAA) was used, though other water-soluble materials can be used as well. The SWNT film was transferred onto this surface (Figure 2-8A), with care taken during the transfer process to use orthogonal solvents that do not dissolve the PAA. Though the PAA layer was initially extremely flat, it is so water soluble that a surface layer was dissolved by the condensation of water vapor from the ambient lab environment during the evaporation of solvents used in the membrane dissolution step of the film transfer. The resolution to this problem was to perform these transfers in a glove bag purged with nitrogen to eliminate the major source of atmospheric water condensation. Following the film transfer from the membrane to the PAA layer, the new top surface of the SWNT film was then coated with a thermoset or a thermoplastic ‘conformal layer,’ initially either molten or a liquid, by sandwiching this material between the SWNT film and a second glass substrate (Figure 2-8B). The thermoset or molten thermoplastic conforms to the SWNT film morphology including particulate protrusions followed by its solidification. The glass/PAA/SWNT film/thermoset/glass sandwich was then submerged into water and the PAA layer dissolved away, exposing the flat SWNT film side bonded via its other side to the thermoset (or thermoplastic) layer on glass.

Figure 2-8. Schematic representation of A) SWNT film transferred to PAA layer, B) with thermoset covering SWNT film and sandwiched with second glass substrate, C) after PAA is washed away and first glass substrate is removed. Note that in C) the setup is rotated. Image is not to scale.
A number of thermoplastic and thermosetting systems were explored as the conformal layer to conform to the protruding features in the SWNT films. Most of these exhibited problems. For example, polydimethylsiloxane (PDMS) underwent significant shrinkage upon curing that built stresses into the material around the particulates in the SWNT films. Combined with the high flexibility of the cured PDMS these stresses displaced the particles into the region where the flatness is desired (Figure 2-9). While this system was a failure, it highlighted the need for a low shrinkage, high durometer system. Other thermosets and thermoplastics worked well, eliminating large wrinkles that were visible on the optical microscope, but proved to be incompatible with the solvents required for subsequently deposited solution processable polymers (Figure 2-10).

![Figure 2-9. AFM image of transferred SWNT film A) using a thermoplastic that had too high a coefficient of thermal expansion, causing wrinkling and >100 nm variations and B) using a thermoset that shrunk during curing, causing stresses and forcing inset particles upwards.](image)

After consulting with numerous manufacturers and experimenting with approximately 10 different thermosets and thermoplastics to determine material
properties, a UV-cured polymer system was identified that was not dissolved in chlorobenzene and seemed to have all the other desired characteristics. Films were transferred as described using this polymer system and it was found that the UV-cured polymer penetrated through the pores of the SWNT film as is shown in Figure 2-11. Organic light emitting diodes made from these samples exhibited extremely low current densities and little luminous output suggesting that the flooded polymer was preventing charge injection into the organic layer. To overcome this issue, the transfer technique was modified by the deposition of a Parylene C protective layer on top of the SWNT film prior to deposition of the UV cure polymer, attempting to form a barrier to prevent the polymer from flooding the surface. This appeared to succeed and the flooding seemed solved; however, devices fabricated on such substrates continued to fail to achieve appreciable current densities or any light emission.

Figure 2-10. A) AFM image of inwards protruding ridge in transferred SWNT with B) a line scan indicating features less than 30 nm. C) The ridge is shown in the optical microscope (with AFM tip during scan) to demonstrate that the size of this feature that can be overcome.
Another possible source of this failure was the presence of water vapor. The dissolution of the PAA layer is a diffusion limited process that took weeks for the 1 inch square substrates used, during which time water diffused into the voids within the SWNT film and the conformal layers. If water vapor remained and later escaped into the organic layers or calcium contact of an OLED, it could poison the contact and inhibit charge injection. To test this, the substrates were baked for 7 days at 130°C under vacuum (~1 Torr) after PAA dissolution in water but prior to OLED fabrication. There was no improvement in device performance.

Discussions with the manufacturer of the UV cure epoxy revealed that there is an oxygen sensitive component that does not cure after exposure to oxygen. The ambient laboratory environment may be creating an incurable component that (despite the Parylene C barrier) slowly works its way into bulk of SWNT film, either limiting charge injection or poisoning the MEH-PPV layer. To avoid this issue, the assembly of the substrate onto the conformal layer and subsequent UV exposure was moved into the inert argon environment of a glove box. This finally enabled some level of luminance and charge injection, but both metrics were 1 – 2 order of magnitudes lower than in conventional devices.

This demonstration of charge injection and luminance was a promising indicator that we were on the right path but perhaps there still was some barrier layer forming. I tested both a brief oxygen plasma ashing as well the local application of high currents through a mercury drop contacting the SWNT film to attempt to remove this barrier, to no avail. Finally, I attempted using a thicker (150 nm) SWNT film so that any problematic materials or epoxy components would have a more tortuous path to the
SWNT surface – though the thicker film would admittedly absorb more light. OLEDs built on these devices demonstrated no shorting, even on devices using 100 nm active layers. The I-V characteristics looked similar to that observed in control ITO OLEDs (Figure 2-10); however, there was no light emission from these devices.

At this stage, we have demonstrated proof-of-principle in a new method of fabricating flat SWNT films that avoid shorting, even in devices using thin active layers. However, after one year of testing approximately ten different thermosets and thermoplastics and overcoming many obstacles, we had failed to find a material that was compatible with both the PAA layer used in the sacrificial transfer and the organic active layer. Though it may be possible that such a material exists, the time intensive optimization process made further pursuit of this technique an ineffective use of effort and this approach was abandoned. Further efforts were focused on means to eliminate the problematic particulates.

Figure 2-11. Amplitude (V) image of flooded SWNT surface demonstrating penetration of UV-cured polymer surrounding SWNTs.
Figure 2-12. Current density of OLEDs with 150 nm MEH-PPV organic layer for SWNT using conformal UV-cure polymer and brief plasma clean to remove barrier (orange) vs. ITO control device (green). It is clear that the devices are not shorted; however while the ITO device achieves >1000 cd/m² luminance, the SWNT device emits no light. This comparison is made to show the similarities in the devices and lack of shorting – a more in-depth description of OLED performance will be discussed in Chapter 5.

Magnetic Purification

After the failure of the conformal layers (which sought to overcome all particulates, regardless of source) in working devices, the remaining efforts were targeted at the specific particulates that remain. Based on observation that many of the remaining particulates were bucky onions with a metallic catalyst core, methods were sought to preferentially eliminate these metallic bucky onions. Attack by acid in this case was not an option because the carbon shell is self satisfied and any means that would damage these objects would likewise damage the SWNTs themselves. A method published by Kim and Luzzi to magnetically purify the sample consisted of filtering the SWNT suspension through iron granules in a strong magnetic field to trap and eliminate the impurities in the strong local magnetic field gradients formed around protrusions in the iron granules.\(^{89}\)
To test the magnetic purification scheme, DPLV grown SWNTs were used that had been pre-purified through two nitric acid reflux and cross-flow filtration cycles to eliminate and break-up the bulk of these bucky onions (Figure 2-13A-B). A magnetic purification was attempted to remove the remaining metal/bucky onion aggregations. A buret (with stopcock) that was 15 mm in diameter was filled to a height of 15 cm with iron granules ~1-2 mm in size. Seven pairs of strong rare earth magnets were placed on the outside of the buret with an alternating polarity such that a locally inhomogeneous field was created through the iron granules. After thoroughly flushing these iron granules with deionized water, the SWNT solution was flowed through the buret at a rate of 4 mL/min.

Dilute films were made from this solution before (Figure 2-13A-D) and after magnetic purification (Figure 2-13E-F). These films were subsequently transferred to copper TEM grids and studied under TEM (Figure 2-14. A-F) imaging and by EDS (Figure 2-14. G-J). These studies demonstrated that most of the metal catalyst particles had been successfully removed by the magnetic purification. The few catalyst particles remaining were typically singular (not in an agglomerate). There did exist many other carbonaceous materials as well as significant levels of iron contaminants that had been introduced during the magnetic purification. To eliminate these iron contaminants, baths in concentrated nitric or hydrochloric acid were used to dissolve the metals with relatively high success as indicated by both TEM imaging and EDS which reveal no evidence of residual iron. Hydrochloric acid can, in theory, contribute to the dedoping of the heavily p-doped SWNTs but these effects were not observed here in UV-Vis spectra or resistance measurements.
The ultimate fatal flaw in these experiments became excessive material loss as well as too many non-metal filled bucky onions that remained. In initial experiments, the SWNT concentration in the solution decreased by several orders of magnitude during the magnetic purification. This was attributed to two causes. First, the use of Triton-X as a non-ionic surfactant is potentially problematic as we were using it at a pH of 10-11. Free ions can interfere with the suspendability of SWNTs in Triton-X and the SWNTs can flock out. To test this idea, an ionic surfactant, sodium cholate, was tested with losses similar to those observed in Triton-X suggesting that the surfactant type does not play a major role.

The second loss mechanism is from the bundling of SWNTs in solution, held together by van der Waals bonds. If bucky onions are bound or trapped in these bundles, as they are magnetically removed the associated nanotube bundles may likewise be removed. Further, as additional SWNTs flow past these trapped bundles, they may also bind to the structures. With many potential trapped bundles, there are opportunities for such losses to occur which could explain the significant reduction in material. Sonication can break apart these bundles but carries the risk of further damaging the SWNTs due the sonochemistry done by the very high energy pulses locally present in cavitation bubbles\textsuperscript{71,77-79}.

Magnetic purification could effectively eliminate many of the problematic catalyst filled bucky onions but it proved labor intensive and led to problematic material loss. These limitations might be acceptable if the resultant material was highly pure; however, even after magnetic purification enough hollow bucky onions remained (Figure 2-15)
that devices made from films of this material continued to exhibit electrical shorts. A more universal purification scheme was needed.

Figure 2-13. A) Height and B) amplitude AFM image of film fabricated from PLV grown SWNTs after undergoing a 45 hour nitric acid reflux (2.6 M) and 27 hours of crossflow filtration. C) Height and D) amplitude image after secondary nitric acid reflux (21 hours, 66 hours total) and secondary crossflow filtration (11 hours, 61 hours total). E) Height and F) amplitude image following magnetic purification. All images show material that has not been centrifuged or filtered (beyond cross-flow). Full height scale in each image is 300nm.
Figure 2-14. A-F) Characteristic TEM images following magnetic purification. Dark particles can still be seen but these are no longer bucky onions. G-J) Examination through energy dispersive spectroscopy (H, J) at points labeled by ‘+’ in G) and I) indicates the introduction of iron during the purification process however this can be removed easily through an acid bath.
Figure 2-15. Hollow bucky onions remain after the metallic, cobalt and nickel catalyst filled bucky onions are removed during the magnetic purification. In these images, the residual iron has been dissolved away in an acid bath.

**High Speed Centrifugation**

Many of the particulates remaining after the nitric acid reflux and cross-flow filtration could be centrifuged out using a relatively low speed centrifugation at 6000 RPM (2500g) in a fixed angle rotor centrifuge; however, there remained a significant
fraction that were not be removed. Early efforts performed twelve, hour-long centrifugations at 6000 RPM, collecting the supernatant after each run. While the first two centrifugation passes showed significant improvement, the process quickly began yielding diminishing returns with little to no improvement in particulate removal by the twelfth pass. Material that had been centrifuged twice was used to create PLEDs that operated using a 250nm spun cast active layer, though shorts still remained and additional centrifugations (up to ten) yielded no additional improvements in terms of working pixel yield.

With repeated centrifugations at 6000 RPM offering little improvement beyond modest initial gains, it became natural to wonder how centrifugation at higher speeds could affect material quality. Ultrahigh speed centrifugation (>100,000 g) has been used to sediment SWNT bundles and nanotube aggregates and isolate individualized carbon nanotubes – though such methods require aggressive sonication to debundle the nanotubes which can be damaging. More recently, moderately high speed centrifugations (20,000 g) have been used to remove carbon nanoparticles and amorphous carbons. By using the same Sorvall centrifuge used for previous centrifugations but changing the rotor out for a different model, rotational speeds of 17,000 RPM (23,000 g) can be achieved – though less than 70 mL can be centrifuged at a time – enough for just a few SWNT films.

To test this high speed centrifugation, material that had been nitric acid refluxed and cross-flow filtered twice was then centrifuged at 17,000 RPM in sequential 1 hour runs with the resultant material being assayed through characterization of thin films of the material largely via optical and atomic force microscopy (AFM) as well as further
characterization by transmission electron microscopy and energy dispersive spectroscopy (EDS). After the first pass, there was a drastic improvement, though a non-negligible fraction of large impurities remained as could be seen in an optical microscope. The second and third centrifugation passes succeeded in eliminating the major fraction of impurities, leaving a film that was particulate-free in ~90% of the 5 x 5 μm² AFM scans taken (Figure 2-16).

High resolution TEM images of the few remaining particulates showed that the major fraction were agglomerates of hollow bucky onions, like those shown in Figure 2-6. As these hollow bucky onions are empty, they are relatively buoyant in solution and are not readily centrifuged away in a standard centrifuge scheme where the sediment, in this case assorted denser carbonaceous impurities and catalyst filled bucky onions, is trapped against the bottom side wall of the centrifuge bottle while the SWNT-rich supernatant – with buoyant bucky onions - is collected for further use (the sediment is discarded). An effort was made to preferentially collect the middle of the suspension, avoiding the top portion where more buoyant objects might be found, but no improvement in high resolution TEM images of these films was found relative to a control sample where both fractions were collected equally.

Despite the few remaining hollow bucky onions, the gains made in this ultrahigh speed centrifugation were impressive and would be beneficial to implement into our standard operating procedure; however, several factors limited its benefit. The largest issue was that the centrifuge rotor was limited in the total mass that could be accelerated to high speeds, meaning that at 17,000 RPM, less than 70 mL (enough for just a few dilute films) can be centrifuged. Larger volumes would require reduction in
centrifugal speeds. Even for lab scale applications, and certainly for industrial scale uses, a means of increasing the throughput was necessary.

The second issue with this small batch centrifugation lay in the handling. After centrifugation was complete, the centrifuge gradually slows to a stop under its own friction over 20 minutes and the centrifuge is opened. The vials must then be carefully removed and moved to the cleanroom where the supernatant is manually pipetted out and collected. Each of these steps introduces external forces and turbulence into the solution in the vial, potentially dislodging the sediment collected at the bottom of the vial and resuspending it with the supernatant. This can be minimized, but not avoided, with repeated centrifugations. For these reasons, a centrifuge that could accelerate a larger volume to high centrifugal speeds while also avoiding the handling issues that limit the efficacy of the fixed angle rotor centrifuge was desired.

![AFM Image of 17000 RPM Centrifuged Material](image)

Figure 2-16. AFM image of 17000 RPM centrifuged material.

**Continuous Flow Centrifugation**

Continuous flow centrifugation, consisting of a hollow rotor spinning relative to stationary inlet and outlet tubing, allows for the high speed centrifugation of an effectively limitless volume of material. It has long been used in micron scale biological
separation applications but has never been demonstrated to be useful in nanoscale separations. The technique offers the advantage of a high throughput, restricted only by the amount of sediment that can be collected in the rotor, while still attaining high centrifugal forces to effect the separation of a sediment from a supernatant solution.

The cross-section of the Thermofisher Contifuge Stratos continuous flow centrifuge rotor is shown in Figure 2-17. The head of the rotor, colored in shades of gray, remains stationary while the remaining components are accelerated in the centrifuge housing and rotate at 17,000 RPM (24,000g). Injection of glycerin into the outer housing forms a liquid seal, creating an air pocket that prevents solution from taking a pathway to escape out of the necessary gaps between the rotating and stationary components. This glycerin seal requires the rotor to be brought to speed empty, followed by injection of solution from the inlet tubing, as indicated in the center of the rotor. The solution flows through the body, with sediment trapped at the outer walls of the rotor body, and the purified solution then flows up and through the outlet where it can be collected and, if desired, passed through again. The volume of material that can be centrifuged is only limited by the lifetime of the bearings and the sediment capacity of the rotor, which in these tests was never appreciably filled.

Tests on the Contifuge continuous flow centrifuge were carried out using material that had undergone two nitric acid refluxes in 2.6 M nitric acid for a total of 70 hours – 50 hours for the first reflux and 20 hours for the second. The material then spent a total of 26 hours in crossflow filtration (20 hours following the first reflux; 5 hours following the second), flushing the material with a total of 73 L of Triton-X buffer (55 L; 18 L). This material was then diluted to a concentration of 7.5 μg/mL – five times more
concentrated than the standard film making concentration – and a film was made to assess initial material quality. As can be seen in Figure 2-18A and 2-19A, this material contains many large particulates that would make successful device fabrication using thin organic layers impossible – though it should be noted that a standard 6000 RPM centrifugation was not used here to provide a more severe test for the new technique.

![Diagram of Contifuge Stratos continuous flow centrifuge.](image)

Figure 2-17. Cross-section view of Contifuge Stratos continuous flow centrifuge.

Two liters of this solution was used as the starting material and was flowed through the continuous flow centrifuge at a speed of 15 mL/min, meaning that it took 16 minutes and 40 seconds for each infinitesimal volume fraction of the material to pass through the 250 mL centrifuge rotor, or put another way, on each pass the material was centrifuged for 16 minutes and 40 seconds (with the exception of the final pass which was carried out at 7.5 mL/min). Following each pass, the material was sonicated for 10
minutes to degas the solution and debundle the nanotubes. Each day (for three days), the solution was passed through the centrifuge four times and after the fourth pass each day, the centrifuge was stopped, the sediment collected and the rotor cleaned. Twelve passes were selected so that the total centrifugation time was on the same order of magnitude as our standard fixed angle rotation time (3 x 1 hour).

To assay material purity, small films were made using a constant volume (1mL on a 17mm diameter film membrane) of the sampled material at the end of selected runs (1st, 3rd, 6th, 12th) and transferred to glass and silicon substrates. Initial studies on these films were carried out using optical microscopy, atomic force microscopy (AFM), UV-Vis spectrophotometry, and resistivity measurements via a van der Pauw four probe station. As can be seen in Figure 2-18 and Figure 2-19, a dramatic improvement is observed after a single pass through the continuous flow centrifuge with further improvement upon further centrifugation cycles. These images, taken using an optical microscope, are intended to provide a feel for the improvement; however with so few particles, a single image cannot convey the cleanliness of the sample as a whole. AFM images are shown in Figure 2-20; however, this is a significantly more local technique and should be viewed in conjunction with the larger area studies of Figures 2-18 and 2-19.

While such assays were reassuring, a more meaningful test of the efficacy of the purification was developed: devices were made to test the frequency of shorts using a simple SWNT / organic semiconductor / gold electrode stack. By applying a voltage between the SWNT film and the gold electrode, it could be determined whether shorting pathways exist between the two electrodes. By varying the thickness of the organic layer, the frequency of these shorting pathways could be determined.
Figure 2-18. Optical microscope (5X objective) image of film made from constant volume of solution (A) before centrifugation and after (B) one pass, (C) three passes, (D) six passes, and (E) twelve passes.

One of our most promising applications, and the focus of Chapters 3 and 4 of this dissertation, is the carbon nanotube enabled vertical organic field effect transistor (CN-VFET). For this reason, the shorting frequency at varying thicknesses was tested using the standard dilute CN-VFET film that is effectively 2 nm thick (the thickness is
estimated by scaling by volume a solution used from a thicker test sample). These films were transferred to p⁺-silicon / SiO₂ (200 nm) / benzocyclobutane (7 nm – this layer, not relevant to these measurements, is discussed further in Chapter 3) substrates with amorphous small molecule ((N,N'-di(1-naphthyl)-N,N'-diphenyl-1,1'-diphenyl-1,4'-

Figure 2-19. Optical microscope image (20X objective) of film made from constant volume of solution (A) before centrifugation and after (B) one pass, (C) three passes, (D) six passes, and (E) twelve passes.
Figure 2-20. AFM images of material after (A) 3 passes through continuous flow centrifuge and (B) 12 passes through continuous flow centrifuge with height scale bar shown to right. Because AFM only investigates relatively small areas, it is limited in its ability to assess film purity over a large sample however the lack of large particulates is promising.

Diamine) or (NPD) was evaporated at thicknesses ranging from 100 nm to 500 nm\textsuperscript{92}. The use of an amorphous material is important because more crystalline organics tend to grow via an island growth mode which leads to pinholes at their grain boundaries and shorting pathways in thin layers that may not be related to the quality of the bottom electrode. NPD was also selected because it possesses a HOMO of $\sim$-5.4 eV, creating
an initial Schottky barrier of ~0.6 eV with the SWNTs which means that there should be little initial charge injection. This barrier means that any significant current is indicative of shorting. Following the NPD layer, gold top electrodes, with an area of 0.035 mm$^2$, were evaporated on top of the organic layer through a TEM grid shadowmask, yielding 40 – 50 testable pixels per device. A standard probe station probe was used to contact the SWNT/gold bottom contact and a gold wire gently contacts the top electrode. For each pixel, approximately 1 V was applied between the electrodes to test whether a shorting current was present. Because of NPD’s large initial barrier, any pixel with a current that measured beyond a few tens of nanoamps was characterized as shorted.

Films that had been centrifuged two times at 6000 RPM and filtered twice through 650 nm pore membranes were used as a control sample to test the conventional purification techniques. In making these films, fabricated on our standard mixed cellulose ester membranes, every precaution was taken to ensure cleanliness in handling including deposition of gold electrodes after transferring the SWNT film to minimize underlying particulates. Despite these precautions, this material possessed a large number of shorts that made the use of organic layers below 400 nm difficult and inconsistent – even when a 2 nm thick SWNT film was used. There were no working pixels at 200nm (0 pixels out of 32) and even at 300 nm, less than half the pixels work (15 pixels out of 32 or 47%). Fortunately, and consistent with previous publications from the group, the yields do improve appreciably when 400 nm (27 out of 32 or 84%) and 500 nm (31 out of 32 or 97%) thick organic layers are used.

Material fabricated from the continuous flow centrifuged material performed considerably better. Table 2-1 shows the working pixel yields for films following the 6$^{th}$
and 12th pass of the continuous flow centrifuge on standard mixed cellulose ester (MCE) membranes as well as a polycarbonate membrane (with ion etched pores) to test whether membrane defects were still playing a role in the presence of shorting pathways. While the yields were quite good (70-75% success rate at 200 nm vs. 0% previously), a few anomalous results stood out. Namely, the similar yields with 200 nm and 300 nm NPD layers in the 12th pass material on an MCE membrane, as well as the seemingly low yield using a 300 nm NPD layer with this material. This suggested that perhaps the particulates were relatively large ones that had fallen on the substrate, an effect that might manifest itself as increased shorting across a range of thicknesses, similar to what was seen here.

Table 2-1. Characterization of SWNT material following continuous flow centrifugation with predeposited electrodes

<table>
<thead>
<tr>
<th>NPD Thickness (nm)</th>
<th>6th pass MCE membrane</th>
<th>12th pass MCE membrane</th>
<th>12th pass Isopore Polycarbonate membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Good</td>
<td>Short</td>
<td>Yield</td>
</tr>
<tr>
<td>200</td>
<td>25</td>
<td>38</td>
<td>40%</td>
</tr>
<tr>
<td>300</td>
<td>64</td>
<td>9</td>
<td>88%</td>
</tr>
<tr>
<td>400</td>
<td>62</td>
<td>0</td>
<td>100%</td>
</tr>
</tbody>
</table>

There was at least one step in which the substrates were exposed to a non-cleanroom environment. These samples had been fabricated following our standard operating procedures which was to predeposit the Cr / Au SWNT contacts. This exposes the substrates to the potentially dirty glovebox before the conductive nanotube film is adhered, allowing for particulates to land on the substrate and force the SWNT film upwards to create shorting pathways. To avoid this potential issue, the experiment was repeated with Au electrodes deposited after transfer of the SWNT film so that any particles would be on top of, rather than underneath, the conductive SWNT film. This
was done with both a dilute, VFET-density (~2 nm effective thickness) SWNT film and a thicker 20 nm thick SWNT film.

Between 32 and 70 pixels were measured on devices for NPD layers ranging from 100 – 250 nm thick and as can be seen in Table 2-2, we really have achieved remarkable levels of purity relative to our previous standards. For NPD layers of 250 nm, we did not observe a single shorted pixel in both the dilute film or in the 20 nm thick film, containing 10 times the quantity of material (and thus 10 times the number of intrinsic particulates per unit area). At 200 nm, where previously no working pixels were observed, we now achieved a >95% success rate in both dilute and 20 nm thick films. The yields did drop with thinner active layers, indicating room for improvement, but even at 100 nm thick organic layers the yield was still 35% in the VFET film – allowing us to build VFETs across a previously inaccessible range of channel thicknesses to probe the physics at work these thinner layers as discussed in Chapter 4.

Table 2-2. Characterization of SWNT material following continuous flow centrifugation with postdeposited electrodes

<table>
<thead>
<tr>
<th>NPD Thickness (nm)</th>
<th>2 nm thick SWNT Film</th>
<th>20 nm Thick SWNT Film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Good</td>
<td>Short</td>
</tr>
<tr>
<td>100</td>
<td>24</td>
<td>43</td>
</tr>
<tr>
<td>150</td>
<td>38</td>
<td>8</td>
</tr>
<tr>
<td>200</td>
<td>65</td>
<td>3</td>
</tr>
<tr>
<td>250</td>
<td>46</td>
<td>0</td>
</tr>
</tbody>
</table>

Further characterization of the material via AFM, TEM and optical microscopy coupled with the high pixel yields of the highly centrifuged material demonstrated that we were eliminating many of the bucky onions and other contaminants from the SWNT material but it did not yield much information on SWNT material losses. To study this, films were made both to determine material losses and to measure the conductivity of
the SWNT films as the material underwent increasing centrifugation (Table 2-3). Films were made on a 17 mm diameter mixed cellulose ester membrane using a controlled amount of solution (collected after the number of centrifugation passes indicated). Four-probe van der Pauw measurements were made on these films to measure sheet resistance followed by optical characterization via UV-Vis transmission spectra and thickness measurements were taken by atomic force microscope (AFM) in which a reliable stepheight was achieved by protecting the nanotube film with photoresist while the surrounding film was removed by ashing in an oxygen barrel ashler (followed by dissolution of the photoresist in acetone). This allows us to study material loss and the conductivity of the film as defined by $\sigma = 1/(R_s \cdot t)$.

The results of these studies are shown in Table 2-3 and Figure 2-21. Material loss is significant, exceeding 50% by the 6th pass through the centrifuge. In early centrifugations, this material loss does not seem to have a significant impact on conductivity. Indeed, after the first centrifugation we even see a slight increase in conductivity. This increase is perhaps not surprising as it can be observed from Figure 2-18 that this first centrifugation pass removed many impurities that may have impeded the conduction pathways between SWNTs.

<table>
<thead>
<tr>
<th>Centrifugation Passes</th>
<th>Volume of Solution (mL)</th>
<th>Thickness (nm)</th>
<th>Loss (%)</th>
<th>Sheet Resistance ($\Omega/\square$)</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>1</td>
<td>43</td>
<td>n/a</td>
<td>70</td>
<td>3322</td>
</tr>
<tr>
<td>1st</td>
<td>1</td>
<td>30</td>
<td>30%</td>
<td>97</td>
<td>3436</td>
</tr>
<tr>
<td>3rd</td>
<td>1.8</td>
<td>48</td>
<td>38%</td>
<td>65</td>
<td>3205</td>
</tr>
<tr>
<td>6th</td>
<td>2.5</td>
<td>48</td>
<td>55%</td>
<td>69</td>
<td>3019</td>
</tr>
<tr>
<td>12th</td>
<td>2.8</td>
<td>52</td>
<td>57%</td>
<td>85</td>
<td>2262</td>
</tr>
</tbody>
</table>
In further centrifugations, as the beneficial effects of removing particulates are reduced and material loss is coming almost entirely from the elimination of nanotubes, the conductivity does begin to suffer. This effect is somewhat surprising; as it implies a preferential loss of long SWNTs or bundles which contribute the most to the conductivity. While material losses were expected, we anticipated that these losses would be distributed evenly and not impact the conductivity of the bulk film. However, it has been reported that bundles of long SWNTs could have an increased density relative to individualized nanotubes if the surfactant molecules are only coating the outer tubes in the bundle, having a less buoyant effect on their density leading to their preferential removal\textsuperscript{37}. There are applications where this preferential bundle removal might be advantageous, most notably the carbon nanotube enabled vertical field effect transistor (Chapter 3-4) where bundled nanotubes can screen the gate field and limit device performance.

The conductivity decrease should not be overstated and it is unlikely that this will be a limiting factor. After six centrifugation passes, the conductivity decrease was less than 10% and analysis of this material shows a high quality film, free of particulates. The improved pixel yield (with an associated performance enhancement that will be detailed in Chapter 4) allows for studies and large area devices that otherwise would be difficult to achieve and as such, the slight loss in conductivity is more than acceptable. While there certainly is room for improvement in the process, the continuous flow centrifuge can serve as a viable technique to achieve highly purified SWNT material on an industrial scale for organic electronic devices.
Figure 2-21. UV-Vis spectra for films made from a constant volume - 1mL solution on a 17mm diameter film membrane.
Overview

The low density of electronic states (DOS) found in carbon nanotubes and graphene near its Dirac point allows for modulation of the Fermi level of these materials in a manner not accessible using conventional metals that possess a high DOS. Recently, such Fermi level tuning was exploited in a novel device architecture: the carbon nanotube enabled vertical field effect transistor (CN-VFET), which demonstrated state-of-the-art current densities at low operating voltages from comparatively low mobility organic semiconductors. Unlike in conventional thin film transistors (TFTs), transconductance arises from a gate field modulation of the contact barrier at the organic semiconductor/nanotube interface – an effect that will be discussed in this chapter.

Figure 3-1A shows a conventional organic TFT. A thin organic channel layer is deposited on top of a gate and gate dielectric with patterned source and drain electrodes defining the channel length. With the source at ground, a potential is applied between the source and gate electrodes inducing charge carriers in a very thin layer within the organic semiconductor, adjacent to the dielectric surface. As a source-drain voltage is applied, these charges move through the organic channel layer giving rise to the device current.

The low mobility of organic semiconductors, typically on the order of $10^{-1} - 10^{-3}$ cm$^2$/V·s, limits the on-currents that can be achieved by these conventional lateral channel TFTs. This can be overcome by the use of long channel widths or short channel lengths but the former makes for large devices, reducing the packing density
and increasing parasitic capacitances, while the latter requires high resolution patterning to define the narrow channel, which becomes cost prohibitive. Unfortunately despite advancements in organic TFTs, the best published on-currents in these devices remain about two orders of magnitude below what can be achieved using alternative competitive technologies such as polycrystalline silicon TFTs\textsuperscript{93, 94}.

The low mobility of organics can be overcome through the novel architecture of the CN-VFET which offers facile control over the channel length. As shown in Figure 3-1B, the device again is built upon a gate and gate dielectric but here the source, channel and drain are all stacked vertically. The source electrode used in the CN-VFET is a dilute (but random) nanotube network that is porous but well above the percolation threshold (Figure 3-1C). For those more familiar with nanotube transistors in which the nanotube itself is the channel\textsuperscript{27, 95, 96}, it may be important to emphasize that the dilute nanotube network here serves only as the source electrode so that no separation of metallic and semiconducting nanotubes is required. The channel length in the CN-VFET becomes simply thickness of the organic material which can be readily controlled by thermal evaporation or spin coating, eliminating the need for lithographic patterning to achieve short channel lengths.

![Figure 3-1. Schematic of A) conventional, lateral channel thin film transistor and B) vertical field effect transistor. C) AFM image of dilute SWNT source electrode.](image-url)
In 2008, Liu et al. published the first CN-VFET that used a dilute nanotube source electrode\(^{30}\). Two years later, with an improved understanding of the essential device parameters, McCarthy et al. reported a high performance CN-VFET that achieved on-currents that were nearly four times better than those reported in conventional TFTs using the same channel material\(^{40,93}\). In 2011, McCarthy et al. integrated the optically transparent drive transistor as a VFET in a vertical stack with the OLED pixel, to demonstrate a vertical organic light emitting transistor emitting light across the full aperture with minimal performance degradation in power consumption, luminance or efficiency\(^{41}\).

The CN-VFET has demonstrated high levels of performance and in this chapter we discuss the underlying device physics. Because the device operates as a Schottky barrier transistor, I will first discuss energy band alignment in the Schottky-Mott model and how low density of state metals (such as carbon nanotubes and graphene) enable a new device mechanism for barrier height modulation and charge injection. As further studied in my work, the device performance also benefits from a barrier width modulation enhanced by the direct gate field access to the low DOS metal/organic semiconductor interface. This is shown for nanotube source electrode based devices in which I changed the nanotube surface density, thereby modifying the screening of the gate field from the relevant interface. I then further elucidated the phenomenon in the first graphene source electrode based VFETs (G-VFETs), in which both continuous graphene and graphene with a variable density of micron scale holes had been created by a novel process.
Energy Band Alignment at a Metal-Semiconductor Interface

**Schottky Barrier Height Modulation**

To first approximation, the work function difference between a metal and a semiconductor dictates the transport across their junction, determining whether the contact will be Ohmic or have a Schottky barrier to electrical transport\(^97-99\). When two such materials are brought into contact, charge flows between them allowing the Fermi levels to align as the system reaches thermal equilibrium. For a conventional metal, possessing a high density of electronic states, the carrier concentration is so large that the Fermi level shift occurs almost entirely in the semiconductor (possessing a comparatively low carrier concentration). In the Schottky-Mott model, this shift creates a Schottky barrier that is equal to the difference between the work function of the metal and the electron affinity of the semiconductor. The large DOS in the metallic electrode serves as a reservoir, requiring the addition/subtraction of large amounts of charge to induce appreciable shifts in its work functions (like the water level in a large lake, much water must be added to change the level perceptibly).

This picture changes dramatically for low DOS metals like carbon nanotubes and graphene for which charge addition/subtraction induces much more dramatic work function, or equivalently, Fermi level shifts (little water must be added to a tall narrow glass to change the level accordingly). Since the Fermi level in these materials can be changed in response to gating fields, these low DOS carbon based metals, placed in contact with a semiconductor, admit a new mechanism for current modulation by the gate field control of their trans-junction transport through tuning of the Schottky barrier height. This additional means of control allows for new high performance device architectures.
Experimental evidence for this mode of barrier height modulation in low DOS materials was first reported by Longeran in 1997 in a tunable diode featuring a hybrid inorganic / organic structure (n-indium phosphide / poly(pyrrole))\textsuperscript{100}. Longeran was able to demonstrate electrochemical manipulation of the work function of the poly(pyrrole) polymer resulting in tuning of the turn-on voltage of this device by more than 0.6 V. In 2004, Wu \textit{et al.} demonstrated Fermi level control in a SWNT film electrode where the application of a gate field led to the depletion of the S1 and M1 van Hove singularities, as measured by optical spectrophotometry, providing strong evidence for a Fermi level shift of more than 0.7 eV\textsuperscript{38}. More recently, Wadhwa \textit{et al.} succeeded in exploiting the low DOS of SWNTs to actively modulate their Fermi level in a gated SWNT / Si Schottky junction solar cell\textsuperscript{29}.

**Schottky Barrier Width Modulation**

It is important to note that an applied gate field can modulate transport across a metal / semiconductor junction even in high DOS metals through band bending, which modulates the Schottky barrier width\textsuperscript{99,101-104}. The application of an appropriate field causes the valence band (highest occupied molecular orbital, or HOMO, in an organic semiconductor) to bend towards its Fermi level, causing the Schottky barrier formed with the metal to thin. The thinning of this barrier in turn enhances the tunneling current across the barrier. Of course, the opposite is also true, by reversing the bias the applied field will induce a widening of the barrier and a reduction of the tunneling current thus allowing for modulation of the device current independent of the barrier height modulation discussed previously. Such a mechanism was exploited by Yang and co-workers in related VFETs that used a partly oxidized aluminum source electrode and required a very high capacitance (supercapacitor) gate dielectric to achieve the reported
performance and others have since extended this work\textsuperscript{101-106}. The CN-VFETs and G-VFETs (with holes) use both mechanisms and thus dramatically outperform metal source electrode based VFET devices.

**Schottky Barrier Modulation in the CN-VFET**

The carbon nanotube-enabled vertical field effect transistor (CN-VFET) acts as a Schottky barrier transistor – transconductance arises via gate field modulation of the Schottky barrier height and width. When there is no applied field, the device sits at thermal equilibrium with the Fermi level of the nanotubes aligned with that of the organic semiconductor. To turn on a CN-VFET with a $p$-type organic channel material, the source electrode is held at ground as a negative voltage is applied to the gate, shifting the Fermi level of the SWNT film down and diminishing the height of the barrier at the SWNT / organic semiconductor interface. Simultaneously, the porous source electrode allows penetration of the gate field to access the nanotube/organic semiconductor interface, bending the highest occupied molecular orbital (HOMO) towards its Fermi level and thinning the Schottky barrier. When a source-drain voltage is applied concurrently, the lowered and thinned barrier allows for high on-currents across the organic channel. Conversely, when a positive gate voltage is applied, the barrier is enhanced and the device is turned off. The energy band alignment and Schottky barrier modulation was previously modeled at the interface of a single, metallic SWNT and a semiconducting polymer channel and the resulting simulation, demonstrating the aforementioned barrier height and width modulation, is reproduced in Figure 3-2\textsuperscript{30}.

It is this combination of both barrier height and width modulation that gives the CN-VFET its dramatic performance advantage over metal source electrode VFETs\textsuperscript{101-105}. The high DOS of the metals used in those devices precludes barrier height modulation...
of the Fermi energy of the metal electrode so that all current modulation arises via gate field modulation of the barrier width.

![Image of energy bands](image)

Figure 3-2. Electrostatic simulation of energy bands at the interface of a single SWNT and the organic channel layer on gate / gate dielectric (inset) under increasing gate voltages. As the gate voltage is increased, the SWNT Fermi energy can be seen to be decreasing in addition to the thinning of the Schottky barrier. Reprinted with permission from Liu et al.30

**Fabrication of Vertical Field Effect Transistors**

Though the materials used for the CN-VFETs and G-VFETs discussed in Chapters 3 and 4 of this dissertation were varied to match the desired experiments, the procedure to fabricate these devices was similar for all and will be briefly described here. A labeled photograph of the structure for visual reference follows at the end of this section (Figure 3-3). Changes to these procedures for individual applications will be noted in the section that their implementation is discussed.

VFETs were fabricated using $p^+$-doped silicon as the gate electrode with a 200 nm SiO$_2$ thermal oxide (Silicon Quest International), diced into 0.6"x0.6" substrates with the
use of a protective photoresist layer during dicing to eliminate adhesion of Si chips to
the surface. The use of this relatively thick gate dielectric necessitates large gate fields,
with gate voltage ranges from -40 V to +40 V, but it has been demonstrated in earlier
work that the use of a thinner and/or higher $k$-dielectric can minimize the gate voltage
range required$^{40,41}$. In some devices, such as the solution processable VFETs in
Chapter 4, this is done using an atomic layer deposition (ALD) grown Al$_2$O$_3$ dielectric
over a metal gate deposited on glass; however, for cost reasons, the rest of the VFETs
demonstrated here will be fabricated on the Si/SiO$_2$ substrates.

A thin, hydrophobizing benzocyclobutane (BCB) layer$^{107,108}$ has been shown to
minimize charge trapping in organic FETs and has reduced hysteresis in previous CN-
VFETs$^{41}$ and is incorporated in all devices described here. BCB (Dow Chemical Co.,
Cyclotene 3022-35), diluted to 1 part in 50 in trimethylbenzene, is spuncast on the
Si/SiO$_2$ at 4000 RPM, resulting in a 7-8 nm thick layer which is hard-baked at 225°C to
cross-link the material and render it resistant to solvents. Gold source contacts (40 nm)
with a chromium layer (10 nm) to promote adhesion to the BCB are thermally
evaporated onto the substrate through a shadow-mask. SWNT films are fabricated on
MCE membranes that are then cut using razor blades into 2 mm strips (two strips per
substrate) and transferred to the substrates by wetting with isopropanol, using the
evaporation of the isopropanol to pull the film into more intimate contact with the surface
to generate strong adhesion via van der Waals forces. The MCE membranes are then
dissolved away with an acetone vapor bath followed by 4 acetone baths with a final
isopropanol bath. Samples are transferred to the glovebox and baked at 225°C to
dedope the $p$-doped SWNTs (doped during the nitric acid reflux) which shifts their Fermi
level to approximately -4.7 eV and generates a larger initial Schottky barrier with most 
$p$-type organics.\textsuperscript{41} The organic semiconductors are then deposited over the entire 
nanotube strip, by thermal evaporation unless otherwise noted. Gold drain electrodes 
are evaporated through a transmission electron microscope (TEM) grid with 100 μm 
hexagonal grid spacings to define a VFET area that is 0.035 mm$^2$ with over 160 VFET 
‘pixels’ per substrate that can be readily split into 4 sections to test 4 variables (with 40 
VFET pixels each) per device.

Gate contact is made by scratching through the dielectric with a scribe and making 
contact with an indium dot. This indium dot and the gold source contact are contacted 
by needle probes and the gold drain electrode is gently contacted via a gold wire. 
Electrical measurement is done on a custom built probe station using a two channel 
Keithley 2612A System Sourcemeter controlled by a program written in LabVIEW (both 
probe station and LabVIEW program were designed by collaborators in the Rinzler 
Laboratory). Though a current is directly measured, this dissertation will give values as 
a current density because, unlike conventional lateral channel TFTs where the current 
scales linearly with the channel width, the current in CN-VFETs scales with the total 
channel area. Areal current density represents a rational and important figure of merit 
to for insight into device performance as in practical applications, such as active matrix 
organic light emitting diode displays, the pixel area is limited by the real estate occupied 
by the driving transistor, impacting device properties such as pixel lifetime and power 
consumption.
Figure 3-3. Labelled layout of CN-VFET on silicon substrate. The dashed line indicated the approximate outline of the SWNT source electrode as the film as the very dilute film is difficult to see (though the reorientation of the pentacene organic layer used here can be observed on the strip to the right).

**Effect of SWNT Film Porosity on VFET Performance**

In the VFET architecture, the use of a porous source electrode allows the gate field to penetrate and access the contact barrier at the source / organic interface. In CN-VFETs, this gate field penetration is permitted by the low areal surface density of the SWNTs on the substrate which can be readily controlled during fabrication of the SWNT film by varying the concentration and/or volume of the SWNT suspension used. The nanotubes are typically bundled and screen the gate field, severely limiting Schottky barrier modulation at increasing SWNT densities\(^{109}\) and mandating the use of dilute SWNT networks. By lowering the SWNT density, we anticipate seeing an
improvement in the device current on-off ratio; however, as the film conductivity is inversely proportional to film density, the increased series resistance may negate the improved gate field penetration and limit on-currents when a dilute network is used. To further elucidate the role that the porosity in the SWNT thin film plays, as well as to fabricate an optimized SWNT film for future device studies, I studied CN-VFET performance as a function of SWNT density.

SWNT films were made at four different characteristic densities / thickness (Figure 3-4) by varying the volume of a standard, dilute SWNT solution used to fabricate the films via vacuum filtration. It was found, via atomic force microscopy (AFM), that 120mL of this solution made a film that was approximately 40 nm thick. Films were then made using 4.8 mL, 7.2 mL, 9.6 mL, and 12 mL of this standard solution for SWNT films that had an effective thickness of 1.6 nm, 2.4 nm, 3.2 nm and 4.0 nm respectively. It should be noted that quoting a “thickness” is somewhat misleading here as all films are too dilute to cover the entire substrate and vary locally from 0 nm to over 10 nm. Nevertheless, an equivalent thickness is the most convenient term to convey the film’s properties and as such it will be used here.

Devices were fabricated as shown in Figure 3-5. Two probe resistance measurements were taken and the sheet resistance of each film was estimated based on the sample geometry (displayed in Figure 3-4) prior to baking and dedoping the film. 460 nm of dinaphtho-[2,3-b:2',3'-f]thieno[3,2-b]-thiophene (DNTT) doped with MoO₃ was grown on the SWNT film to serve as the channel layer. DNTT is a recently developed, air stable small molecule that is chosen for its relatively high mobility (2.9 cm²/V·s) and deep HOMO level of -5.4 eV which creates an initial energy barrier of ~0.7 eV\textsuperscript{110}. 

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Figure 3-4. AFM scans of increasing film densities used to probe effect of SWNT film porosity with estimated sheet resistance measurement. The same SWNT material was used for all films. All SWNT films are limited by impedance at tube-tube junctions; however, as the number of long conductive pathways across the substrate is diminished, this impedance begins to drastically limit conductivity in very dilute films.
For each film density, a minimum of seven pixels were measured with representative data plotted in Figure 3-6. At high SWNT densities, screening limits device performance and current modulation in both the on- and off-state current. As the SWNT film density is decreased, the on-state current initially increases as the gate field is allowed to penetrate the porous SWNT film. This on-current is maximized at the 2.4 nm equivalent film, after which it becomes limited by the high resistivity of the nanotube film due to the limited conductive pathways across the device – indicated by the linear on-current even at low source-drain voltages. Though the on-current becomes limited, the on-off ratio is maximized due to the enhanced gating and the lower off-state in this dilute network. As the order of magnitude gain in on-off ratio is more important for potential device applications than the fractional reduction in on-current, we chose to use the more dilute film to explore future CN-VFET devices.

These results are indicative of the balance that must be struck in VFET source electrodes. As source electrodes become more porous, the enhanced gate field penetration leads to improved device performance; however, past a certain threshold, we begin to pay a high cost with regards to series resistance. More conductive
electrodes, such as graphene, should enable high levels of performance by avoiding the resistivity and screening effects found in dilute networks.

Figure 3-6. CN-VFETs with a 500 DNTT channel using SWNT films of varying thicknesses. A) Transfer curves, B) output curves on a linear scale, C) current on/off ratio, and D) output curves on a logarithmic scale for films of varying densities. Devices with thin SWNT films turn on faster and are more fully off but may become limited by the high resistance of the SWNT film.

Graphene-Based Vertical Field Effect Transistors

The use of a graphene electrode in vertical field effect transistors should offer advantages over thin films of carbon nanotubes that may afford not only improved performance but also a solid test bed in which to study the physics that occur at the
source-channel interface. Similar to carbon nanotubes, graphene has a low density of states near its Dirac point that should lend itself well to modulation by an external gate field. The monolithic nature of graphene also offers a natural advantage in sheet resistance relative to dilute SWNT networks where impedance at tube-tube junctions dominates performance, particularly as the films are made more dilute. The planar structure of graphene also can afford many other advantages by allowing thinner channel layers (and proportional increases in on-currents) and enhanced reorientation of the small molecule channel layers. It has been demonstrated that some organic molecules will preferentially π-stack on the pristine sidewall of a SWNT, reorienting it such that the high mobility direction is vertical, facilitating high performance CN-VFETs. As the anisotropy with molecular orientation can lead to orders of magnitude differences in the mobility of an organic material, this reorientation can yield essential improvements in device performance. Graphene is structurally similar to the nanotube sidewall and should induce similar reorientation, but where the bundling, curvature and high porosity of nanotube networks contributed to mixed crystalline phases, the planar graphene should lead to a more uniform structure in the channel layer.

Graphene also offers a unique window into the device physics at play in the VFET architecture. As has been discussed, both Schottky barrier height and width modulation contribute to current modulation in a VFET. The nanotube based devices operate in a mixed fashion, taking advantage of both modes. As depicted in Figure 3-7Bb, the continuous electrode provided by graphene can probe (principally) the effect of the barrier height modulation by screening the gate field and preventing it from inducing barrier width modulation at graphene / organic interface. By then purposely introducing
holes in the continuous graphene electrode to allow gate field access (Figure 3-7Bc), it becomes possible to probe both modes in a single material system.

The G-VFET device architecture is shown in Figure 3-7A (discussed below). The thin channel layer between the graphene source and top drain electrodes imposes rather severe requirements on the quality of the graphene layer, at least in terms of minimizing vertical protrusions. The conventional polymethylmethacrylate (PMMA) transfer method\textsuperscript{10} for copper-based chemical vapor deposition (CVD) grown graphene was found to be unreliable, with numerous tears and wrinkles causing frequent shorting pathways\textsuperscript{15, 112}. Techniques described in the literature to improve the polymethylmethacrylate (PMMA, Microchem 11\% in anisole) transfer were tried, however, these did not fully eliminate damage induced by the swelling of the PMMA during acetone dissolution.\textsuperscript{15, 112} A modified PMMA transfer method was developed that gave much better results. Transfer of CVD grown graphene from the copper growth substrate was improved by depositing a thin layer (\textless{} 100 nm) of Au as a protective layer before spinning the PMMA support film, ensuring a post-transfer surface that is free of difficult to remove polymeric residue. The thin metallic layer avoids strain induced by the swelling of the PMMA film during the more conventional transfer process. This is especially important at domain boundaries where chemical bonding between the polymeric chains and the graphene is favorable.\textsuperscript{113}

Figure 3-7C illustrates the procedure for transferring and patterning the graphene using an Au thin-film as a protective layer and etch mask. Gold was thermally evaporated at a thickness ranging from 20 to 100 nm through a rectangular shadow mask onto the graphene grown on polished copper foils by Max Lemaitre at the
FIGURE 3-7. (A) G-VFET architecture and drive scheme. (B) Energy level diagram for a GVFET at the graphene-semiconducting channel interface for constant drain voltage and three distinct gate voltages. The black line depicts the hole injection barrier and depletion layer in the semiconductor for a continuous graphene electrode. The red dashed line depicts the same features for the case of a graphene electrode perforated with holes. For the continuous graphene case current modulation is due principally to barrier height lowering (thermionic emission). For the perforated graphene case the barrier also thins (enhancing tunneling). (a) Initial Schottky barrier and band bending induced by the offset of the graphene work function with the HOMO level of the organic semiconductor. (b) Moderately reduced Schottky barrier height resulting from the shift in the graphene work function. Band bending is less pronounced for the continuous graphene. (c) At high gate voltage the barrier height is significantly reduced and the depletion width thinned for the case of perforated graphene. (C) Schematic of the graphene source electrode fabrication process using a protective evaporated Au layer. (i) the Au film evaporated onto the as-grown graphene on Cu, (ii) the PMMA spin coated onto the gold layer, (iii) Cu etched away, (iv) graphene/Au/PMMA stack adhered to SiO$_2$ substrate, (v) PMMA etched away in O$_2$ plasma, (vi) Au film etched away leaving behind a residue-free, perforated graphene sheet.
Nanoscale Research Facility, followed by spin coating the PMMA and baking. After copper dissolution in a perchloric solution (Transene, APD-100), the Au coated section of the graphene/Au/PMMA sandwich was adhered, graphene side down, to the p^+-Si/SiO\textsubscript{2}/BCB substrate through pressure applied by handclamps for four hours in an 80°C oven. After baking in a tube furnace for one hour, the Au served as an etch mask while the PMMA and excess graphene around the gold mask were dry-etched in an O\textsubscript{2}\textsuperscript{−} plasma (1 hour, 600sccm, 600 W) thus defining the edge of the graphene source electrode. An iodide based gold etchant (Transene, Au TFA Etchant) subsequently removed the mask layer. Finally, a gold source contact was evaporated along one edge of the graphene layer completing the source electrode. Note than unlike in the CN-VFET, here the gold source contacts are evaporated after the graphene source electrode was transferred as the etchant that removes the graphene mask would also attack these electrodes.

Micron scale holes with a crudely controlled density were produced in the graphene by varying the thickness of the Au mask layer. Thin Au layers possess sub-micron pinholes, with a through-hole density that depends on the layer thickness. During the dry etch of the PMMA, reactive oxygen radicals penetrate these holes to etch the graphene and underlying BCB, leaving behind circular holes in the graphene with an average diameter of 2-3 microns. The diameters of these holes are self-limiting due to the increasing diffusion path length for counter propagating oxygen and reaction products in the confined space between the Au and the SiO\textsubscript{2}, as the etched region grows. The measured areal hole densities in the graphene used to build the G-VFETs
discussed below were 0, 2, 13 and 20% with average hole diameters of \(2.2 \pm 0.6\mu m\), \(2.3 \pm 0.6\mu m\), \(2.5 \pm 1.0\mu m\), respectively.

Figure 3-8 compares the quality of the graphene transferred with and without the use of a 100 nm (pinhole free) protective Au layer. Raman spectroscopy provides a comparative measure of graphitic materials, capable of distinguishing single-layer graphene from multi-layer graphene and graphite\(^{18}\), and characterizing disorder, crystalline grain size, stacking symmetry, and doping of the graphene films\(^{114-116}\). The D to G-band intensity ratios are shown versus the FWHM of the 2D-band overtone for 100 distinct points for the graphene films transferred with and without the use of the gold protective layer. The D-band was below the noise threshold, and the 2D-FWHM was substantially reduced in the majority of measured spots for the Au protected films.

![Image](image-url)

**FIGURE 3-8.** (A) Raman spectral data in the form of a cluster plot of D/G peak ratios versus the 2D-band FWHMs for a graphene layer transferred using the Au protected process (black squares) and a graphene layer transferred using the conventional PMMA process (red triangles). One hundred point were recorded on each layer in a square array of points having a pitch of approximately 50 \(\mu m\). A smaller D/G ratio and FWHM are desirable, as seen for the majority of points recorded for the Au-transferred layer. (B) SEM (scale bars: 2um) and (C) AFM images (15 x 15 \(\mu m\)) of graphene layers transferred to SiO\(_2\) using the Au-protected and the conventional PMMA processes, as indicated by the labels.

Scanning electron (SEM) and atomic force micrographs (AFM) of films transferred by
the two methods are shown in Figures 3-8B & 3-8C, respectively. The films transferred using the gold protective layer are continuous, without the polymer residue, micro-tears, and wrinkles characteristic of the standard PMMA transfer.

The organic semiconductor channel layer evaporated onto the graphene was dinaphtho-[2,3-b:2',3'-f]thieno[3,2-b]-thiophene (DNTT)\textsuperscript{110}. The flatness of a single layer of graphene should in principle permit even sub-100 nm channel layer thickness (with corresponding performance enhancement) without incurring electrical shorts to the top drain electrode. We found however that device yields suffered when the DNTT thickness was below 250 nm. This may be a consequence of the low surface energy of graphene and crystallinity of DNTT that results in island growth incorporating pinholes and shorting paths to the subsequently deposited Au drain electrode, for thin channel layers. To ensure effectively 100% yields and to permit a direct performance comparison against comparable channel thickness CN-VFETs, a DNTT channel thickness of 500 nm was used.

G-VFET devices were tested with the graphene source electrode contact held at ground potential, while the drain and gate were biased relative to ground. Figure 3-9 shows typical output curves for the G-VFETs with graphene source electrode areal hole densities of 0, 2, 13 and 20% (Figure 3-9A). Both the on ($V_G=-40$ V) and off ($V_G=+40$ V) states are shown. The advantage of the short channel length in the vertical architecture is seen in the high on-current densities at low drain voltages ($\leq |5|$ V). The on-current densities clearly scale with the density of holes in the graphene source electrode. Figure 3-9C plots the on/off current ratio of the devices as a function of the on-current density (as the drain voltages are swept from 0 to -5 V). The 20% areal hole density electrode
yields on/off ratios exceeding $10^6$. Attempts to get higher hole densities (>20%) by making the protective Au layer thinner resulted in discontinuous graphene sheets. Ordered hole arrays would avoid this problem and provide a path for further device optimization. A summary of the device characteristics versus areal hole density is plotted in Figure 3-9D.

FIGURE 3-9. (A) 50 x 50 µm SEM images of the transferred graphene films having the indicated hole densities. (B) G-VFET output curves for the off-state ($V_G = +40V$) and the on-state ($V_G = -40V$) for these graphene source electrode hole densities. (C) On/Off current ratio versus on-state current density up to a drain voltage of -5V for each hole density. (D) On-current densities and On/Off current ratios for drain voltage up to 10 V versus source electrode hole density. 3 orders of magnitude current modulation is achieved in the pore-free g-VFET with an additional 3 orders of magnitude improvement upon introduction of pores.

The current modulation seen to occur in the continuous graphene electrode (over three orders of magnitude) provides strong support for the anticipated Schottky barrier height modulation (changing principally the thermionic emission) in the low DOS metal. Introducing 20% holes into the graphene source electrode yields a further 2-3 decades
of transconductance, resulting from tunneling through the barrier. Extrapolating from the Kevin probe measurements of Yu et al.\textsuperscript{117}, we estimate that our gate sweep results in a 0.4-0.5eV shift of the graphene work function and a commensurate modulation of the barrier height. Since tunneling currents also depend strongly on barrier height (e.g. within the WKB approximation \( j \propto e^{-}\frac{\hbar v_{F} z}{2e}\)), such modulation can explain the dramatic performance advantage these low DOS metals have over conventional metal source electrode devices.

Comparison between the G-VFET and CN-VFET reveals differences that can be attributed to the morphological differences between the respective source electrodes. Figure 3-10A compares transfer curves for a G-VFET with a 20\% areal hole density graphene source electrode and a typical CN-VFET fabricated on the same p\textsuperscript{+}-Si/SiO\textsubscript{2}/BCB gate electrode/gate dielectric substrates. The drain voltages are adjusted to yield comparable on currents at a gate voltage of -40 V. The large hysteresis seen in the nanotube based device has been explained by ambipolar charge traps in the BCB having a well-defined critical field for charge exchange with the electrode\textsuperscript{118}. This hysteresis can be minimized by restricting the gate voltage range but here it is interesting to observe the significantly smaller hysteresis for the graphene source electrode over the same large voltage range. This is likely due to the enhanced field concentration around the nanometer width nanotube electrodes versus the semi-planar graphene electrode in the vicinity of a hole.

Output curves for the two devices are plotted in Figure 3-10B for gate voltages of ±40V and drain voltages out to -10V. Compared to the nanotube device the graphene devices exhibits a drain voltage delay of ~500 mV before current begins to flow. This is
likely due to the work function difference between the graphene (-4.6 eV) and the DNTT (-5.4 eV) generating a larger initial barrier than that between the DNTT and the nanotubes. The nitric acid purification of the nanotubes charge transfer dopes them, placing their work function around -4.9 eV, after which a heating step dedopes them to an estimated -4.7 to -4.8 eV. The field concentration around the nanotubes may also give them an advantage in terms of this lower turn-on voltage. As the drain voltage continues to grow, the nanotube device off-current begins to suffer as the drain field concentration around the nanotubes begins to extract charge despite the off state (+40 V) gate voltage. The planar graphene does not exhibit such degradation in the off state. The graphene electrode also excels in the on-state at high drain voltage. At $V_D = -10V$ the CN-VFET on-current density is $\sim 300mA/cm^2$ compared to an astounding $\sim 1200mA/cm^2$ for the graphene device. We attribute this to the lower impedance of the monolithic graphene layer versus the dilute nanotube electrode. Figure 3-10C compares the on/off ratios for the two devices as a function of their on-currents ($V_G = -40V$) as the drain voltage is swept from 0 to -10 V. The impedance limited on-current and increasing off-current degrades the on/off ratio of the nanotubes device while that of the graphene device remains above $10^6$ out to -10 V.
FIGURE 3-10. Comparison of graphene and carbon nanotube enabled VFETs with all other device layers the same. (A) Transfer curves for a CN-VFET and the G-VFET with a 20% areal hole density electrode. (B) Output curves for both devices in the on ($V_G = -40\, \text{V}$) and off ($V_G = +40\, \text{V}$) states up to $V_D = -10\, \text{V}$. (C) On/Off ratios versus on-current density for drain voltages to -10V. Morphological differences in the two devices allow for faster turn-on by the CN-VFET but higher on-currents in the G-VFET due to the lower sheet resistance.
CHAPTER 4
DEVICE PHYSICS OF VERTICAL FIELD EFFECT TRANSISTORS WITH VARYING
CHANNEL PROPERTIES

Overview

In Chapter 3 I introduced the structure of the vertical field effect transistor (VFET) and discussed its operation as a Schottky barrier transistor using porous, low density of state materials. In this chapter, I detail investigations into the role of the organic channel using highly purified SWNT material to achieve the thinnest channels yet in a CN-VFET. Additionally, I have achieved state-of-the-art performance in a low voltage, P3HT transistor by demonstrating the first solution processable CN-VFET which could open pathways to manufacture via inexpensive inkjet printing of the devices. Finally, I used C$_{60}$ to create an $n$-type VFET, with potential applications in CMOS-like inverters, and test our understanding of how variation of device parameters, such as the work function of the drain electrode and of the SWNT film, can alter the energy band alignment and impact device performance.

Role of Channel Layer Thickness in Vertical Field Effect Transistors

Though the VFET architecture allows facile fabrication of channel lengths down to the nanometer-scale, particulates in the SWNT source electrode have traditionally led to poor device yields below 400 nm thick channels and effectively zero working VFETs sub-250 nm (see Chapter 2). While the incorporation of 500 nm channel lengths has enabled state-of-the-art organic FET performance$^{40}$, even thinner channel layers should offer further enhancements in the device on-currents. With the use of the continuous flow centrifuge purification technique discussed in Chapter 2, high purity nanotube films were available that enable working VFETs with channel layers as thin as 100 nm. The
high quality of this material offers the opportunity to study the effect of channel thickness in a range that was previously inaccessible.

The selection of an appropriate organic small molecule channel material is important as the channel is thinned. Many of the crystalline organic materials possessing (relatively) high mobilities have been shown to reorient on the nanotube sidewall, leading to a high surface roughness and non-uniform channel thicknesses. For very thin channel layers, the low surface energy surface offered by the SWNT sidewall can also yield island growth that does not create a uniform, pinhole-free film until relatively thick films are grown.

For this experiment, N,N'-di(1-naphthyl)-N,N'-diphenyl-1,1'-diphenyl-1,4'-diamine) (NPD) was used as for the channel layer (Figure 4-1). NPD is a small molecule organic material with a HOMO of -5.4 eV that is often used as a hole transport layer. As an amorphous material, NPD should create a relatively uniform layer on the BCB / SWNT surface.

The NPD CN-VFET device structure is shown in Figure 4-1B. Dilute SWNT films were fabricated using the continuous flow centrifuged material discussed in Chapter 2 (12 passes through the continuous flow centrifuge); however to achieve the very sparse / porous films required here, one part of the SWNT solution was diluted in ten parts deionized water allowing for more uniform films yet very thin films. Though the initial material was in a 1% Triton-X solution, deionized water (filtered through a 50nm pore, hollow fiber filter) was used for the dilution to avoid the introduction of new contaminants that might come with a fresh Triton-X solution that had not been centrifuged. Despite the dilution, the solution remained about an order of magnitude above the critical micelle
concentration required to suspend SWNTs in Triton-X which was calculated to be around 0.013%. Films were estimated by atomic force microscope (AFM) and sheet resistance measurements to be of approximately the same nanotube density as our standard VFET films – though a small deviation from the standard film density is difficult to avoid.

![Figure 4-1](image_url)  
**Figure 4-1.** Structure of A) NPD and B) NPD CN-VFETs with varying channel thicknesses.

Contrary to standard procedure, the dilute SWNT films were transferred to Si/SiO$_2$/BCB substrates *prior* to growing the gold source electrode so that any contamination during processing steps in the glove box would be on top of, rather than below, the nanotube film and would be less likely to short. Nonconductive particles underneath the conductive SWNT film can create shorting pathways through thin devices; however, if these particle land on top of an already transferred SWNT film, shorting can likely be avoided (though shadowed regions may still prove problematic). In devices using a 200 nm NPD active layer, transferring the SWNT films prior to growing gold source electrodes increased the working pixel yield from 70% (with predeposited Au source contacts) to 96% (with postdeposited Au source contacts).
Following transfer of SWNT films, NPD was thermally evaporated onto the device. Each Si/SiO$_2$/BCB/SWNT substrate can be divided into four quadrants (see Figure 3-3 for reference) and the channel can be grown independently in each quadrant by masking off the other regions. Therefore, 100 nm, 150 nm, 200 nm and 250 nm NPD VFETs were all fabricated on a single substrate while 300 nm and 500 nm NPD VFETs were grown on a second substrate (and fabricated on a different day). The VFET stack was capped by a 30 nm Au thermally evaporated drain electrode with 40 nm Au source contacts grown on the SWNT film at the end of device fabrication.

Output curves are shown for these devices are shown in Figure 4-2. As can be seen, thinning the channel layer yields significant enhancements in the device on-currents (Figure 4-2A,B). The device with a 100 nm channel thickness reaches 110 mA/cm$^2$ at 5 V, 50 times more than the current density achieved by the 500 nm device (2.2 mA/cm$^2$) and 2.5 times more than the 150 nm device (44 mA/cm$^2$) despite a reduction in the channel thickness of only a third. However, this increase in the on-current density also coincides with a reduction in the off-current density for thin channel layers, though the off-state does not begin to suffer until the channel reaches approximately 150 nm. The on/off current ratio is shown in Figure 4-2D where the balance between these high on-currents and reduced off-currents becomes more evident. Transfer curves for these devices, where the source-drain voltage was held constant while gate-source voltage was swept across an 80 V range, are shown in Figure 4-3.

These drastic improvements demonstrate the value of the purification techniques discussed in Chapter 2. With the low mobility of organic semiconductors, output
currents in organic TFTs are still 1 – 2 orders of magnitude below those achievable by polycrystalline silicon\textsuperscript{93, 111, 119}, the thin channel lengths of VFETs offer a means to bridge this performance gap. In future VFETs, the use of this highly purified material in conjunction with higher mobility organic materials should facilitate the development of even higher performing CN and graphene enabled VFETs.

Figure 4-2. CN-VFETs with an NPD channel layer of varying thicknesses. Output curves in the on-state ($V_G = -40$ V) on a A) logarithmic and B) linear scale as well as in the C) off-state ($V_G = 40$ V) plotted on a logarithmic scale. D) On/off current ratio – found by dividing the most on-state ($V_G = -40$ V) output curve by the most off-state ($V_G = 40$ V) output curve – plotted against the on-current density. Significant enhancements in on-currents can be achieved through the use of thinner channel layers – though off-currents may suffer.
Figure 4-3. Transfer curves in which the gate voltage is swept while the source-drain voltage is held constant at the voltage indicated. On-current density ($V_G = -40$ V) was meant to be equal for all thicknesses to allow for a more meaningful comparison.

**CN-VFETs with a Solution Processable Channel Layer**

Previous efforts involving CN-VFETs have focused primarily on the use of small organic molecules as the organic channel with early efforts to use polymeric materials yielding devices operating at levels below those required for use in commercial applications. In this work, we seek to extend the materials accessible for use in the CN-VFET architecture to include solution processable polymers. Such devices would enable the advancement of this technology to a state in which printable CN-VFETs could be readily processed for mass market electronics.

Poly(3-hexylthiophene) (P3HT) is a readily available, solution processable polymer frequently used in polymer-based TFTs. The mobility of P3HT, though heavily dependent on factors such as molecular weight, regioregularity and ordering of the polymer, can reach values of up to 0.3 cm$^2$/V·s. Further, the HOMO level of P3HT (-5.2 eV) is sufficiently deep to create a relatively large initial Schottky barrier...
with a dedoped SWNT film so that the device can be sufficiently turned off, even as bundles of SWNTs may introduce screening effects.

P3HT has been used previously in the VFET architecture in devices that used a thin, partly oxidized aluminum source electrode and an ultra high capacitance gate that relied on mobile ions\textsuperscript{102}. Switching speed is limited in such devices by the ionic mobility and the best on/off current ratio reported was $10^3$. As shown below, the P3HT channel CN-VFET does considerably better.

The device layout is as depicted in Figure 4-4. The gate dielectric can have a large impact on device characteristics; here we use an aluminum gate with a atomic layer deposited (ALD) Al$_2$O$_3$ dielectric layer of approximately 25 nm, prepared by thermally evaporating 40nm of aluminum onto glass substrates followed by oxygen plasma ashing to create an approximately 5 nm thick alumina oxide layer. To ensure a robust dielectric layer free of leakage pathways, an additional 20nm of alumina oxide was grown via atomic layer deposition. The resultant dielectric layer had a capacitance of 300 nF / cm$^2$. The BCB layer and transfer of SWNT films (using material that had been centrifuged at 17000 RPM in a fixed angle rotor) was carried out as described previously.

Solutions were made by dissolving P3HT (Sepiolid, Rieke Metals, > 98% regioregular, $M_w < 50,000$) in 1,2-dichlorobenzene at a concentration of 30 mg/mL and stirring overnight. Under an inert argon environment, the solutions were then spun cast on the substrates at 600 RPM while the sample was simultaneously heated to approximately 80 °C by illumination from a heat lamp, yielding a film that measured 325 nm thick. There was no thermal anneal following the spin coating. To complete the
device, 40 nm of gold was evaporated on top of this stack through a TEM grid (100 hexagonal mesh), defining a .035mm$^2$ pad to serve as the drain electrode.

![Schematic of P3HT-based CN-VFET with AFM image of SWNT film superimposed over BCB layer to depict transferred SWNT film.](image)

Transfer and output curves were measured under an argon environment using a Keithley dual channel sourcemeter (Model 2612) controlled by a custom LabView program. Transfer curves for a P3HT CN-VFET held at a constant source-drain voltage while sweeping the gate voltage from -3 V to +3 V and back are shown in Figure 4-6A. There is very little hysteresis shown in these devices. Over this 6 V range in gate voltage, the on-off ratio remains above $10^4$ for all drain voltages up to -2 V.

Figure 4-5 shows output characteristics for this same device, measured by sweeping the source-drain voltage from 0 V to -3 V at gate voltages from +3 V to -3 V, stepping in 1 V increments with a maximum output current density of 84.5 mA/cm$^2$ at $V_{SD} = -3$ V in the most on state. The on/off ratio, found by dividing the most on output curve (-3 V) by the most off output curve (+3 V), is plotted versus on-current density as the drain voltage is swept from 0 to -3 V in Figure 4-5C. Though it does drop with
Figure 4-5. CN-VFETs using a P3HT channel layer. (A) Transfer curve of the CN-VFET over a 6 V range, beginning at $V_G=-3\,\text{V}$, at decreasing drain voltages. Little hysteresis is observed but follows the path indicated by the arrows. (B) Output curves at gate voltages from $3\,\text{V}$ to $-3\,\text{V}$ in $1\,\text{V}$ increments. (C) On / Off ratio found by dividing the most on current ($V_G=-3\,\text{V}$) by the most off current ($V_G=3\,\text{V}$) and plotted against the most on current. On / Off ratio stays above $10^4$ past $40\,\text{mA/cm}^2$.

Increasing voltage, the on/off ratio exceeds $10^4$ through $40\,\text{mA/cm}^2$, falling to approximately $4 \times 10^3$ at the peak current of $84.5\,\text{mA/cm}^2$ ($V_{SD} = -3\,\text{V}$).

Though the vast majority of published P3HT TFTs require voltages that are more than an order of magnitude greater than this CN-VFET, Table 4-1 compares device performance for published P3HT devices operating at less than 5 V. As the difference
in how current is measured in conventional TFTs and VFETs makes direct comparison difficult, it is necessary to convert the linear current density of conventional TFTs into an effective areal current density ($J_{\text{eff}}$), as introduced previously by McCarthy et al. $J_{\text{eff}}$ is calculated from by assuming an interdigitated source-drain electrode pattern in which the source and drain electrodes are patterned to the same width as the channel length in the TFT, thereby maintaining the minimum feature size of the device, such that

$$J_{\text{eff}} = \frac{I_D}{2W \times L}$$

where $W$ and $L$ represent the channel width and length respectively. The P3HT CN-VFET achieves the highest areal current density of these low voltage devices with roughly comparable on-off ratio. This current density is more than enough for practical applications; if the P3HT CN-VFET were used to drive a OLED with a luminance efficiency of 5 cd/A, then a current density of just 20 mA/cm$^2$, achievable at a drain voltage of -1.2 V ($V_G = -3$ V), would be required achieve a luminance of 1000 cd/m$^2$.

Table 4-1. Comparison of P3HT CN-VFET to published, low voltage (<5 V) P3HT TFTs

<table>
<thead>
<tr>
<th>Ref</th>
<th>Device Type</th>
<th>Capacitance (nF/cm$^2$)</th>
<th>Operating $V_{SD}$ (V)</th>
<th>Channel Length (μm)</th>
<th>$J_{\text{EFF}}$ (mA/cm$^2$)</th>
<th>$I_{\text{ON}}$ / $I_{\text{OFF}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>TFT</td>
<td>392</td>
<td>5</td>
<td>7</td>
<td>20</td>
<td>$10^4$</td>
</tr>
<tr>
<td>8</td>
<td>TFT</td>
<td>750</td>
<td>5</td>
<td>5</td>
<td>38</td>
<td>$10^3$</td>
</tr>
<tr>
<td>9</td>
<td>TFT</td>
<td>250</td>
<td>2.2</td>
<td>60</td>
<td>0.025</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>TFT</td>
<td>188</td>
<td>3</td>
<td>10</td>
<td>10</td>
<td>$&lt;10^2$</td>
</tr>
<tr>
<td>11</td>
<td>TFT</td>
<td>332</td>
<td>4</td>
<td>30</td>
<td>1.1</td>
<td>150</td>
</tr>
<tr>
<td>12</td>
<td>Metal Base</td>
<td>n/a</td>
<td>1.2</td>
<td>0.12</td>
<td>10</td>
<td>$10^3$-$10^4$</td>
</tr>
<tr>
<td>3</td>
<td>VFET</td>
<td>1000</td>
<td>5</td>
<td>-</td>
<td>17</td>
<td>$10^3$</td>
</tr>
<tr>
<td>This</td>
<td>CN-VFET</td>
<td>150</td>
<td>3</td>
<td>0.325</td>
<td>84.5</td>
<td>$10^3$-$10^4$</td>
</tr>
<tr>
<td>Work</td>
<td>CN-VFET</td>
<td>150</td>
<td>3</td>
<td>0.325</td>
<td>84.5</td>
<td>$10^3$-$10^4$</td>
</tr>
</tbody>
</table>
An important aspect of the operation of the CN-VFET is that, while current in conventional lateral channel TFTs flows parallel to the substrate, in a CN-VFET current flows in the direction perpendicular to the problem. This is potentially problematic as many organic molecules and polymers demonstrate an anisotropy in their mobility with conventional TFT materials taking advantage of molecules in which the high mobility direction is along the substrate surface. Fortunately, it has been demonstrated that some organic molecules will preferentially π-stack on the pristine sidewall of a SWNT, reorienting it such that the high mobility direction is now vertical, facilitating high performance CN-VFETs\textsuperscript{111}.

Such a reorientation is desired in P3HT on the SWNT film; however, while the lamella of the P3HT polymer suggest the potential for π-stacking on the SWNT sidewall, it is unclear if such a process will occur in a spuncast polymer. Previous studies have shown that the anisotropy between the mobility in P3HT when the (100) plane is oriented parallel to the substrate surface measured along and when the (010) plane is oriented in this direction can give rise to two orders of magnitude difference in carrier mobility between the two directions\textsuperscript{108}. For regioregular P3HT, the (100) plane typically lays parallel to the substrate surface and can have mobilities on the order of several tenths of a cm\textsuperscript{2}/V·s; the highly (>98%) regioregular P3HT used in this study has a stated field effect mobility of 0.2 – 0.3 cm\textsuperscript{2}/V·s in the high mobility plane.

To study whether there is any reorientation of the P3HT as has been observed in small molecule devices, we extract the P3HT mobility using the Mott-Gurney equation in the space charge limited (SCL) regime following methods described previously\textsuperscript{111} though the extracted SCL mobility may vary from the field effect (FE) mobility measured
in conventional TFTs\textsuperscript{131} and make comparison to literature difficult. As the resistance of the dilute CNT film dominates the relationship between drain voltage and current density at high voltages, the mobility cannot be obtained directly from CN-VFETs. Instead, the CNT film was transferred onto a more highly conducting ITO electrode thereby eliminating the film series resistance. Since the device possessed no gate electrode to reduce the contact barrier between the nanotubes and the subsequent P3HT layer alternative means was needed to attain the Ohmic contact between them. To provide the needed Ohmic contact a thin, 1 nm interfacial layer of molybdenum oxide (MoOx) was evaporated between the CNT film and the spuncast P3HT layer. A second 1 nm MoOx layer was evaporated on top of the P3HT followed by a 40 nm Au drain electrode. J-V curves were recorded and fit to the space charge limited Mott-Gurney equation:

\[
J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \tag{Eq. 4-1}
\]

where \(\mu\) is the mobility, \(L\) the thickness, and \(\varepsilon_r\) is the relative permittivity of the P3HT. The latter was determined by measuring the parallel plate capacitance of the P3HT film sandwiched between Al electrodes using an HP 4284A Precision LCR meter.

In contrast with previous studies involving thermally evaporated small molecule VFETs, we do not see any evidence of a reorientation of P3HT on the SWNT film — though it is important to note that the MoOx may interfere with the reorientation. Unlike those systems, where conjugated organic molecules have been shown to \(\pi\) stack on the carbon nanotube side wall such that the high mobility direction grows vertically rather than horizontally, there is no evidence of such a process occurring here. Indeed,
measurement of the mobility of P3HT films spuncast on both ITO and dilute SWNT networks, yielded comparable values of approximately $3 \times 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$ for both devices. At two orders of magnitude less than the manufacturer stated mobility of 0.2 - 0.3 cm$^2$/V·s (admittedly not the most reliable of values), this result may confirm that there is no reorientation of P3HT lamellae on a SWNT film though more study into the difference between SCL and FE mobilities might prove insightful. Efforts to induce reorientation via thermal annealing yielded no improvement in device performance.

Despite the low mobility of P3HT in the vertical direction, we have fabricated solution processable CN-VFET channel layers that achieve high currents at low operating voltages. With future materials that either reorient on the nanotube sidewall or naturally possess high mobility in the vertical direction, we anticipate that solution processable channel layers will prove to be a viable option for future VFETs and VOLETs, opening manufacturing avenues such as facile inkjet printing fabrication.

**n-Type Vertical Field Effect Transistors**

Despite significant research in organic TFTs, the majority of the materials studied have largely (though certainly not exclusively) focused on $p$-type materials. There are many reasons for this, largely due to the lack of appropriate, stable $n$-type materials tied to the poor electrochemical properties of known electron-accepting materials. Despite this lack of attention, $n$-type transistors are essential to the development of complementary logic circuits and as such it is important to develop these materials.

There have been previous forays into $n$-type VFETs. The first published VFET, featuring a copper / aluminum source, demonstrated strong performance using a C$_{60}$ channel layer to achieve high on-currents and on-off ratios of more than $10^6$.$^{101}$ Another patterned VFET using a gold source electrode demonstrated much lower levels
of performance, achieving on-current densities of less than 1 mA/cm² at 10V\textsuperscript{103, 104}. Additionally, Bo Liu demonstrated ambipolar behavior in a CN-VFET using a poly(9,9-diocyl-fluorene-co-N-(4-butylphenyl)-diphenylamine) / [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blend in which the PCBM acted as the \textit{n}-type channel. The \textit{n}-type performance in this CN-VFET only achieved on-off ratios of ~100 so an improved \textit{n}-type material was desired as a first step towards a VFET-based inverter\textsuperscript{109}.

CN-VFETs were made using triply sublimed C\textsubscript{60} as the channel material – thermally evaporated in a 450 – 500 nm thick layer to make VFETs of the structure shown in Figure 4-6. As C\textsubscript{60} is an \textit{n}-type semiconductor (LUMO = -3.7 eV, HOMO = -7.0 eV)\textsuperscript{94, 132}, the energy band alignment varies from the more typical CN-VFET structures which have largely been studied using \textit{p}-type materials – offering a new system to test and advance our understanding of device parameters. It has been demonstrated that for \textit{p}-type channels, baking of the SWNT film prior to device fabrication dedopes the intrinsically \textit{p}-doped SWNTs, shifting the nanotube work function from approximately \textbf{-4.9 eV} to approximately \textbf{-4.7 eV} and generating an enhanced initial barrier to turn the device more fully off\textsuperscript{40}. However, for an \textit{n}-type material such as C\textsubscript{60}, baking may make it more difficult to turn the device off as the barrier here will be diminished by baking – though the very large initial barrier with C\textsubscript{60} may make the small shifts(0.1 – 0.2 eV) irrelevant.

In a separate experiment published in his dissertation,\textsuperscript{109} Bo Liu demonstrated that for devices using a \textit{p}-type channel (poly[[9,9-dioctyl-fluorenyl-2,7-diyl]-alt-co-(9-hexyl-3,6-carbazole)] or (PF-9HK)), the use of a higher work function metal enhanced device performance by increasing device on-currents and decreasing off-currents at a given
voltage. The enhanced on-currents were attributed to a diminished hole extraction barrier at the organic / metal interface with increasing work function metals. It was not clear why the off-currents were increased in lower work function metals, though it was proposed that the increased reverse injection of electrons into the LUMO may have played a role. Here I revisit both of these experiments (regarding the effects of baking and drain electrode selection) using C_{60} to explore these parameters in an n-type VFET.

Figure 4-7 shows typical output and transfer curves for CN-VFETs that have been baked to 225°C followed by deposition of a 450 nm C_{60} channel and either an aluminum (work function = -4.3 eV^{133}) or gold drain electrode (work function = -5.1 eV^{133}). Though both devices perform well, devices using an aluminum drain electrode achieved higher on-currents and lower off-currents. The enhanced on-currents can be explained by a smaller hole extraction barrier at the C_{60} / Al contact; however, similar to the studies by Liu, this makes it difficult to explain the higher off-currents in the Au-based device. The reverse injection in these devices were measured (Figure 4-8) by applying a negative source-drain bias at varying gate fields and a higher current in the reverse direction was observed – perhaps a contributing factor.

To probe the effects of baking on device performance, CN-VFETs were made with a baked (dedoped) SWNT film as well as a non-baked film. These devices again had a 450 nm C_{60} layer and a 40 nm Al top electrode was used. In this experiment, the baked film generally performed better except at high voltages (Figure 4-9). This may be explained by the large initial barrier between the SWNTs and C_{60}, allowing the device to be reliably off so the slightly diminished barrier is not a major issue in the dedoped film until at higher voltages, where we do begin to see the off-current creep up. The device
did turn on a little faster so it seems that the reduced barrier may contribute in this regard. At high temperatures (>600°C) baking has been demonstrated to help to remove contaminants and coatings on the SWNT sidewall, leaving a more pristine surface that could also benefit charge injection. This may have been occurring here as well, though at 225°C it seems unlikely.

These C$_{60}$-based devices should enable the development of CN-VFET based CMOS-like inverters and ring oscillators. The large initial Schottky barrier to electron injection does appear to inhibit device performance and require relatively large source-drain voltages, particularly compared to earlier VFET work by Ma and Yang\textsuperscript{101} which incorporated a porous aluminum (work function = -4.1 eV\textsuperscript{134}) source electrode for a smaller initial barrier. Though these devices do not benefit from Schottky barrier height modulation, the smaller initial barrier appears to compensate for this. This idea is further strengthened by comparisons to work by Tessler\textsuperscript{103, 104}, where the use of a patterned Au source (work function = -5.1 eV\textsuperscript{134}) with an even larger initial barrier achieves two orders of magnitude less current at 10 V than in the CN-VFET. Future studies of materials with smaller initial barriers should enhance device performance.

Figure 4-6. Schematic of C$_{60}$-based CN-VFET with AFM image of SWNT film superimposed over BCB layer to depict transferred SWNT film.
Figure 4-7. Device data for CN-VFETs with a 450 nm C$_{60}$ active layer and either Au or Al drain electrodes, as indicated. The smaller barrier formed with Al demonstrates improved performance in these devices, though the difference is small.

Figure 4-8. Reverse injection in CN-VFETs with a 450 nm C$_{60}$ active layer and either Au or Al drain electrodes, as indicated.
Figure 4-9. Device data for CN-VFETs with a 450 nm C$_{60}$ active layer and 40 nm Al drain electrode. Devices were either not baked or baked to 225°C prior to C$_{60}$ deposition. Here baking improves device performance.
CHAPTER 5
ORGANIC LIGHT EMITTING DIODES USING THIN FILMS OF SINGLE WALLED CARBON NANOTUBES AS ANODES

Introduction

While the principle of electroluminescence in organic materials has been known since the early 1950s\textsuperscript{135, 136}, it was the discovery of the modern, efficient organic light emitting diode (OLED) by Tang and Van Slyke in 1987\textsuperscript{137} that sparked a flurry of research into this organic electronic device structure\textsuperscript{138}. Research in the field has yielded insights into organic semiconductors as well as into the charge injection and transport processes in organic electronic devices that have benefited not only the development of OLEDs but also our understanding of organic semiconductors. Progress in OLEDs has led to the development of an array of consumer technologies that incorporate OLED displays including phones, watches, media players and televisions that offer richer colors, wider viewing angles and lower power consumption.

Research in OLEDs has focused largely on the organic active layers and electron-injecting cathode as the stringent requirements demanded by the transparent, hole-injecting anode has restricted the range of materials available for this electrode. To date, no clear cut alternative to the same transparent conducting oxides (such as tin-doped indium oxide (ITO)) used in the first modern OLED has been found. As the world’s supply of indium dwindles, the push for research into alternative anode materials has grown in recent years. Thin films of single walled carbon nanotubes possess many similar optical and electrical properties and offer a potential alternative to ITO. Further, the large surface area of the porous SWNT film and low density of states suggest ways in which the properties of the SWNT film might contribute to increased charge injection
and better band alignment. In this chapter I will discuss organic light emitting diodes that incorporate these SWNT thin films and compare these devices to ITO.

**Theoretical Background**

All OLEDs operate on the same fundamental principles requiring the simultaneous injection of oppositely charged carriers (electrons and holes) into an organic electroluminescent layer where they recombine to form an exciton which may radiatively decay into an emitted photon\(^1\). While more advanced designs may include one or more additional hole/electron transport/blocking layers to improve the efficiency of this process through charge confinement, the most basic design requires only an anode for hole-injection and a cathode for electron-injection sandwiching the electroluminescent layer (Figure 5-1A). This is basic the structure that will be the focus of this chapter.

There are several important physical properties of these materials involved that will dictate both the efficiency of these processes and the voltages required to drive this process. Both the anode and cathode possess a work functions, \(\varphi\), the energy required to remove an electron from the interior of a solid to the vacuum level (Figure 5-1B)\(^2\). The electroluminescent material is characterized by the energy of its lowest unoccupied molecular orbital (LUMO) in its conduction band and its highest occupied molecular orbital (HOMO) in its valence band, analogous to the electron affinity and ionization potential respectively in inorganic crystalline semiconductors. In an ideal OLED, it is desirable to align the HOMO with the work function of the anode and the LUMO with the work function of the cathode. Differences between these can create a potential barrier to charge injection that must be overcome by tunneling through the barrier as dictated by Fowler-Nordheim tunneling theory\(^3, 4, 5\).
When the materials are brought together, thermodynamic equilibrium requires charge exchange that brings the work function of the anode, cathode and the Fermi energy of the electroluminescent layer into alignment (as discussed in great depth in Chapter 3)\textsuperscript{143}. Under the application of a bias voltage, an electric field is created which reduces the barrier to charge injection. At sufficiently high field strengths, holes are injected from the anode while electrons are injected simultaneously from the cathode into the HOMO and LUMO, respectively, of the electroluminescent layer (Fig 5-1C)\textsuperscript{142}. For polymeric electroluminescent layers, charge transport occurs via site to site hopping along the polymer chain through the active layer (Fig 5-1D). This process occurs rapidly and the holes and electrons combine within the active layer to form an exciton (Fig 5-1E). This exciton can decay radiatively to emit a photon of light (Fig 5-1F) or non-radiatively in which case the excess energy is released as heat\textsuperscript{139}.

Figure 5-1. Schematic of OLED operation\textsuperscript{144}. 
The electroluminescent and charge transporting layers can be either polymeric or small molecule layers and significant research has gone into the study and optimization of these materials as well as the electron injection cathode (for clarification, polymer light emitting diodes are sometimes referred to as PLEDs; however, here I will use the more general term of OLEDs for both device types). Despite the wealth of research in these areas, limited progress has been made in the study of novel anodes beyond transparent conductive oxides – despite known limitations with these materials\textsuperscript{145}. The lack of progress here may be largely due to a lack of materials that can meet the stringent set of requirements imposed upon the anode, such as high conductivity, optical transparency and a high work function, which has limited the opportunity for anodes composed of most materials other than the transparent conducting oxides such as tin-doped indium oxide (ITO) conventionally used in OLEDs. Some progress has been made in the use of conductive polymeric anodes; however the low mobility of most organics, typically less than 1 cm\textsuperscript{2}/V·s, has limited their viability\textsuperscript{146-149}.

Thin films of single walled carbon nanotubes (SWNTs) have been proposed as alternative anode materials for their high work function, considerable conductivity and transparency throughout the visible spectra\textsuperscript{38}. In 2006, three papers\textsuperscript{46, 63, 150} were published reporting the performance of OLEDs using thin films of SWNTs as the anode. Each study noted the difficulty in dealing with the large surface roughness of the SWNT film and attempted to overcome this roughness by planarizing the nanostructured film. Two of the studies applied a water based planarizing layer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) to the SWNT film\textsuperscript{63, 150}. This decreased the surface roughness but the aqueous solution likely did not
penetrate well into the hydrophobic nanotube film, though in one of the papers the authors did blend the aqueous PEDOT:PSS solution with methanol to enhance this wetting. The third effort used an evaporated insulating layer which may degrade charge injection and also used an evaporated small molecule organic layer which would only coat the surface of the SWNT film. In these reports, and others published since, carbon nanotube-based devices have failed to outperform ITO control samples (except with regards to flexibility) but these tests have often treated SWNT films similarly to ITO, not fully exploiting the large surface and low density of states of SWNT thin films.

It has been demonstrated in double layer capacitance measurements that the porosity of a 50 nm SWNT films enhances the accessible surface area by a factor of 2.5 relative to a planar electrode which could significantly enhance performance and light emission. The use of a single layer OLED structure that incorporates a polymeric active layer should permit penetration of the organic material into the SWNT film to access this surface area. In this work, I will examine what effect, if any, a SWNT thin film has on single layer organic light emitting diodes.

**Technical Approach**

Prepatterned ITO on glass substrates, with an ITO thickness of 150 nm and a sheet resistance of 10 Ω/□, were purchased from VisionTek. Prior to their use, the ITO slides were first cleaned by lightly scrubbing with alconox followed by acetone and methanol rinses. The ITO slides then underwent an oxygen plasma ashing (3 min, 300 W, 300 sccm) to render it hydrophilic, eliminate any organic contaminants and modify the surface layer to improve hole injection. A thin (~40 nm) p-type hole conducting polymer, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS,
Baytron P AL-4083, 0.45 micron filtered) was spuncast on the ITO surface at 4000 RPM to prevent shorting by ITO spikes and also to further improve the hole injection from the ITO into the organic layer by lowering the barrier height at this interface (work function of -5.1 eV)\textsuperscript{154-156}. Following a 2 hour bake at 120°C to dry the PEDOT:PSS layer, these ITO substrates were transferred to an argon glovebox for OLED fabrication (Figure 5-2A).

SWNT films were fabricated at a thickness of 50 nm (unless otherwise noted) on mixed cellulose ester membranes using methods described previously in this document and elsewhere\textsuperscript{38} and transferred to glass slides with predeposited gold or palladium electrodes (40 nm) on top of a chromium adhesion layer (10 nm). The SWNT films were cut to the same pattern as the ITO and transferred to glass substrates and brought into the glovebox for device fabrication (Figure 5-2B). The PEDOT:PSS layer was intentionally omitted from these SWNT film-based devices to allow the polymeric layers direct access to the large surface area of the SWNT film.

Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) is a conductive, light-emitting polymer that has been thoroughly studied for over two decades\textsuperscript{157} and was chosen as the electroactive layer for its well-known properties on ITO which allowed for a meaningful comparison with the properties of the SWNT film. With a HOMO around -5.3 eV, MEH-PPV offers a relatively small barrier to charge injection and has a band gap of ~2.3 eV for an orange emission\textsuperscript{158}. Aromatic solvents have been shown to improve polymer/anode contact and electrical conduction in MEH-PPV and so MEH-PPV was dissolved in chlorobenzene\textsuperscript{159}. This solution was then spun onto the SWNT or ITO/PEDOT-PSS surface, forming an electroactive layer of a
thickness that was controlled by varying either the spin speed or polymer concentration. Calcium electrodes (10nm, evaporation rate:1 Å/s), serving as the cathode with a work function of 2.9 eV\textsuperscript{142}, were thermally evaporated onto the MEH-PPV and topped by a thermally evaporated aluminum layer (75 nm, 2 Å/s) to prevent oxidation of the calcium. The area of the Ca/Al pixel was defined by a shadow mask during thermal evaporation to be 8 mm\textsuperscript{2} with eight pixels per device (Figure 5-2C).

Organic light emitting diodes were fabricated and measured under the inert argon environment of a glove box (Figure 5-2D). MEH-PPV was wiped off of the gold electrodes and contact was made to the sample using a sample holder custom made sample holder. Voltage was supplied by a Keithley 2400 power meter and measurement was carried out by a handheld Minolta colorimeter (measured through the glass) or using an Ocean Optics fiber optic spectrometer that was manipulated and aligned with a micrometer inside of a custom built, light-tight box that was anodized to minimize reflected light. For these OLEDs data was taken by hand.

![Figure 5-2. Structure of A) ITO and B) SWNT-based MEH-PPV OLEDs. Photograph of OLED layout from C) top view and D) emitting light under applied voltage.](image_url)
Results and Discussion

Initial MEH-PPV OLEDs were built both on ITO/PEDOT:PSS and SWNT films using MEH-PPV dissolved in chlorobenzene at a concentration of 5 mg/mL and spuncast at 1000 RPM to achieve film thicknesses of 100 nm. The ITO-based devices performed very well under such conditions, achieving maximum luminance values of over 14,000 cd/m² (Figure 5-3), as measured by the Ocean Optics fiber optic spectrometer, far exceeding the requirements of most applications which is approximately 100 – 500 cd/m² for displays. Unfortunately, every SWNT-based device fabricated with 100 nm organic active layers shorted without any light emission.

Figure 5-3. Luminance (blue, left axis) and current density (orange, right axis) of ITO device using a 100 nm MEH-PPV layer.

Post-failure optical microscopy revealed localized, clearly demarcated circular patterns with black spots at their centers and in many cases tracks typical for electrical breakdown. These suggested the existence of localized conductive high spots in the SWNT anode leading to locally thin anode to cathode distances in the devices causing these failures. AFM of the bare SWNT anodes indeed showed locally high features sufficiently tall to penetrate through the relatively thin MEH-PPV organic layer and
directly contact the Ca cathode, creating a direct shorting pathway through which the current could entirely bypass the photoluminescent layer. These features arose from an array of sources (discussed in Chapter 2) including particulates and ridges in the SWNT film where material had accumulated in scratches in the membrane (as shown in Figure 2-5B-C). These shorts made fabrication of SWNT-based OLEDs using a 100 nm active layer impossible and prompted the purification work that is the focus of Chapter 2.

The complexity of the purification of SWNTs made it clear that highly pure SWNT material would not be immediately available (indeed, it wound up taking three years – significantly longer than initially anticipated). In order to allow the OLED project to move forward, a thicker MEH-PPV layer was used to overcome these local protrusions. To cast layers that could be up to 500 nm thick, the concentration of MEH-PPV in chlorobenzene was increased to 10 mg/mL (twice the initial concentration). The significant viscosity of this solution prompted concerns that this new solution would not penetrate the SWNT film and fail to take advantage of the large available surface area. To promote this penetration and help build a thick MEH-PPV layer that more completely covered all parts of the SWNT film, the spincoating procedure was modified from a single spin to three sequential spins at increasing concentrations – 1 mg/mL, 5 mg/mL and 7.5 mg/mL or 10 mg/mL – with a 15 minute bake at 55°C ($T_g$ of MEH-PPV = 65°C$^{160}$) in between spins to dry the organic active layer and drive off residual solvent.

The use of these thicker layers largely overcame the observed shorting pathways and permitted the fabrication of both SWNT and ITO-based OLEDs that used these thicker layers. On a typical SWNT device with eight pixels, there still were frequently 3-
4 pixels that were either partially or fully shorted but enough working devices could be fabricated to test the films and gain some preliminary experience with the OLED.

The SWNT film for these devices was made using material that had been centrifuged twice at 6000 RPM and filtered twice through 0.65 micron filtration membranes and then vacuum filtered on Sterlitech membranes and transferred to glass. Spins of MEH-PPV in chlorobenzene at increasing concentration (1 mg/mL, 5 mg/mL and 7.5 mg/mL) created a film that was roughly 200 nm thick. As shown in Figure 5-4, the best SWNT-based devices consistently achieved nearly twice the luminance achieved in the ITO control OLED at comparable current densities – yielding more than a factor of two improvement in the maximum current efficiency of the SWNT-based OLED relative to ITO (1.5 cd/A vs. 0.74 cd/A). These results appeared to be a confirmation of the potential benefits of the SWNT film.

![Figure 5-4](image)

Figure 5-4. A) Luminance and B) Current Density for MEH-PPV OLEDs using thick active layers and SWNT material that had been twice centrifuged at 6000 RPM and filtered. Here the SWNT based OLEDs achieve twice the luminance at comparable current densities as in the ITO device.

There were two major caveats to these results that could not be neglected. First, though the SWNT film-based OLED outperformed its ITO counterpart when thick MEH-
PPV layers were used, the best ITO devices using thinner MEH-PPV layers were still a factor of 3-4 better. Secondly, the extremely rough SWNT film has many locations where local high spots thin the organic layer so that the effective MEH-PPV thickness might be substantially thinner on the SWNT-based device than in OLEDs using ITO, which could account for the improved performance observed. While these initial results were promising, it became clear that a true comparison would require the use of optimized, thin organic active layers.

The success of the continuous flow centrifuge (Chapter 2) in generating highly purified material allowed for a more meaningful comparison to be attempted. SWNT films using this material were made at thicknesses of 20 nm and 40 nm and transferred as described previously (with the exception of the gold contacts to the SWNT film which were deposited after transfer of the SWNT film to avoid the introduction of particulates in the glove box environment). Following the same procedures as were used previously, thick MEH-PPV OLEDs were made on these films and on an ITO substrate. The MEH-PPV thickness was measured just adjacent to the SWNT film by scratching through the MEH-PPV / Ca / Al electrode using a razor blade. The metal coated region was used to limit stretching of the MEH-PPV film during scratching. An AFM stepheight was taken and it was found that the film was approximately 200 nm thick above each anode – that is to say that the MEH-PPV layer was 240 nm thick on the 40 nm SWNT substrate which suggests that the cathode should sit 200 nm above the 40 nm SWNT film, and similarly for the 20 nm SWNT film and ITO electrode. It should be noted that there is significant variability in the measured thicknesses and in a few regions the MEH-PPV layer on the 40 nm SWNT film was 40 - 50 nm thicker.
In these devices that incorporate the use of highly purified SWNT material, OLEDs using ITO and both 20 nm and 40 nm SWNT films performed nearly identically. Representative pixels are plotted in Figure 5-5 and, in contrast to previous experiments, show nearly identical luminance values and current densities in all three devices. Accepting that the MEH-PPV film thicknesses are indeed comparable, there does not appear to be any improvement arising from the enhanced surface area of the 40 nm thick film. Similarly, the roughly comparable turn-on voltage that can be observed in Figure 5-5D suggests a lack of enhanced energy alignment in these SWNT-based devices (the earlier turn-on that appears present in the 20 nm thick SWNT device is likely due to a leakage current that remains in shorting pathways). Additionally, even with this more highly purified material, the SWNT-based devices still begins to show shorting currents when organic layers below 200 nm are used while the performance of the ITO-based devices improve. This suggests that the roughness of the SWNT films may still be contributing to an effective thinning of the organic layer even in the devices using a 200 nm thick active layer shown in Figure 5-5.

Conclusions

Though SWNT-based OLEDs have achieved results comparable to ITO devices using thick organic layers, a fair comparison in optimized devices is made impossible by particulates in the SWNT film. Though further purification may improve these results, at present, it appears that SWNT-based OLEDs must incorporate the planarizing layers demonstrated in literature. Though SWNT films may enabled some unique or novel designs such as flexible OLEDs and, if sufficiently n-doped, may ultimate prove useful for cathode applications in transparent OLEDs, there does not appear to be an advantage to the use of SWNT films for traditional OLEDs.
Figure 5-5. Results for ITO and SWNT-based MEH-PPV OLED using highly centrifuged material including A) luminance, B) current density (linear scale), C) current efficiency and D) current density (log scale). As can be seen, the devices perform comparably when this more highly purified material is used.
Overview

A light emitting electrochemical cell (LEC) is a solid state electrochemical device in which light emission occurs via the formation of $p$-$n$ junction in a redox reaction. Though LECs share an apparently similar structure and performance characteristics to those found in organic light emitting diodes, the device mechanisms are fundamentally different and insensitive to either the active layer thickness or electrode work functions. This offers an exciting opportunity for transparent thin films of SWNTs serve as both electrodes in a dual emissive device. Here I discuss the fabrication of two types of LECs using thin conductive films of SWNTs as the transparent electrode. First I studied a conventional LEC using a SWNT film to replace the more traditional ITO electrode that emits light in a single direction in a structure similar to the OLEDs discussed previously. After this single emissive device, I fabricated a more revolutionary structure in which I took advantage of the flexibility of a thin SWNT film on plastic to demonstrate a dual emissive device that emits light in both the forward and reverse directions.

Operating Principles and Scientific Background

Light emitting electrochemical cells (LECs) are made up of two electrodes sandwiching an electroactive layer that is comprised of an intermixed blend of a luminescent conjugated polymer and an electrolyte (Figure 6-1A). As voltage is applied across the two electrodes, the mobile ions contained in the electrolyte redistribute and form an electric double layers at the electrode / polymer interface. Once the applied voltage exceeds the polymer’s HOMO-LUMO gap, electrons can be injected into the conjugated polymer and are electrostatically compensated by...
counterions from the electrolyte, p-doping the region adjacent to the anode and doping the opposite region adjacent to the cathode to be n-type. As the electrical conductivity of polymeric materials increases with doping concentration, these layers create a low-resistance contact at the polymer/electrode interface. This highly conductive doped region grows with time and allows for the migration of holes and electrons, driven by the voltage induced electric field, towards the center of the cell where they meet in a thin insulating layer to create an electrochemically induced p-i-n junction in which electrons and holes combine and radiatively decay to emit light (Figure 6-1C).

Figure 6-1. Operational mechanism for a light emitting electrochemical cell. a) Structure of typical LEC with two electrodes sandwiching an electroactive layer comprised of a blend of conjugated luminescent polymer and a solid electrolyte. b) After bias voltage is applied the electroluminescent polymer is oxidized or reduced adjacent to opposite electrodes, leading to the introduction of p- and n-type carriers, compensated by counterions from the electrolyte. c) Charge carriers are driven by the induced electric field towards the opposite electrode and meet to create an electrochemically induced p-i-n junction in which electrons and holes combine and radiatively decay to emit light.

As the LECs rely on the growth and electrochemical doping of these p- and n-regions (which can be thought of as the extension of an optimized anode and cathode)
to drive light emission, the device itself is relatively insensitive to the work function of either the anode or the cathode. This allows an LEC to operate under either forward or reverse bias and furthermore allows for the same electrode material to act as both anode and cathode. This has been demonstrated in several lateral channel LECs with coplanar electrodes but most readily deposited materials accessible in a standard LEC architecture do not possess sufficient transparency for light emission. Materials that do possess this transparency, such as transparent conducting oxides like ITO, are typically sputtered and become difficult to deposit on top of a polymer layer without damaging or overheating the polymer unless advanced techniques are used. SWNTs do not require energetic deposition techniques and their mechanical flexibility should allow thin films of SWNTs to be laminated on top of the polymer layer. This enables a device in which the SWNT thin film can act as both transmissive anode and cathode to allow light emission through each for a dual emitting device.

The highly conductive, doped regions also make LECs relatively insensitive to film thickness as has been demonstrated in devices that used a millimeter-sized lateral gap between coplanar electrodes. Though the turn-on time, limited by ionic mobilities which are significantly lower than electronic mobilities, does increase substantially in these thicker devices (over 5 minutes in devices with a 1 mm gap), it does not appear that other device metrics suffer by using thicker active layers. This offers an opportunity to overcome the shorting pathways in carbon nanotube thin films by using thicker active layers without compromising performance.

Though LECs do not have as extensive a background of scientific research as can be found in the OLED literature, the field has progressed significantly since pioneering
work in the field was introduced by Alan Heeger’s group at UNIAX beginning in 1995\textsuperscript{161, 162, 171}. Since this time, there has been steady research into the operational mechanisms, device structure and interplay of the components that make up the electroactive layer. Due to the insensitivity of the LEC to the work function of the electrodes, the area of alternative electrodes has been the subject of greater inquiry than was observed in OLEDs where the demands are more restrictive and limit material selection. Though at the time that this research project began there was no existing literature on either SWNT-based LECs or dual emissive devices, within six months of the project commencing and shortly after we achieved our first working devices, two independent reports were published of devices discussing dual emissive LECs incorporating carbon-based electrodes – one on SWNT films and one using graphene. In November of 2009 the group of Qibing Pei (one of the inventors of the LEC) published a transparent, dual emissive device formed by the lamination of two thin SWNT films on PET sandwiching the electroluminescent layer\textsuperscript{43}. A few months later, Matyba \textit{et al.} from the group of Ludvig Edman, published dual emissive devices using graphene and PEDOT:PSS as the two transparent electrodes\textsuperscript{172}. Incidentally, the first authors from both papers presented their work at that year’s MRS conference where I also presented my preliminary work on dual emissive devices. Since this sudden burst of independent publication, there have been several related follow-ups,\textsuperscript{173-175} limiting the uniqueness of the research done here.

**Single Emissive Devices**

**Experimental Methods**

Polymer light emitting electrochemical cells that emit light in a single direction were fabricated in a device structure similar to that used for organic light emitting diodes and
shown in Figure 6-2. 50 nm thick SWNT films were fabricated on a mixed cellulose ester (MCE) membrane via vacuum filtration as described in Chapter 1 and transferred to glass substrates with predeposited gold electrodes (with a chromium adhesion layer). Prepatterned ITO substrates were purchased from VisionTek with an ITO thickness of 150 nm and a sheet resistance of 10 Ω/□. These slides were cleaned using alconox followed by acetone and methanol rinses. As a hole transport layer serves little purpose in a light emitting electrochemical cell, no PEDOT:PSS layer was spun cast on the ITO substrate. All steps after substrate cleaning / preparation were carried out in the inert argon environment of a glovebox.

For the electrochemiluminescent layer, MEH-PPV was again used as the emissive conjugated polymer and was admixed with poly(ethylene oxide) (PEO) complexed with a salt, lithium triflate (LiOTf), to serve as the polyelectrolyte. MEH-PPV was used as received; however, the PEO and LiOTf underwent a vacuum anneal to remove any adsorbed water. Master solutions of each were made in cyclohexanone at concentrations of 10 mg/mL for MEH-PPV and 20 mg/mL each for PEO and LiOTf – with heating of the PEO solution to 50°C necessary to get the material to go into solution. From these master solutions, blend solutions were made at a 1:1:0.20 (MEH-PPV:PEO:LiOTf) weight ratio. This blend solution is further split and diluted with pure cyclohexanone by a factor of 10 for one solution and a factor of 2 for the second with some solution remaining at full concentration. These solutions were spuncast at 1000 RPM onto the ITO and SWNT substrates in three sequential steps, starting with the most dilute solution and increasing in concentration, with a 50°C thermal anneal between each step to dry the film. These multiple spins were used to build up the film
thickness to 300 – 350 nm (to overcome protrusions in the SWNT film) with the initial dilute spins enhancing penetration into the porous SWNT film. On top of this polymer / electrolyte layer was evaporated 75 nm of aluminum with a shadowmask defining an 8 mm² active area. Devices were measured in a custom made sample holder using a Keithley 2400 Sourcemeter and a Minolta Colorimeter inside a light-tight box.

Figure 6-2. Device schematic for ITO and SWNT film based light emitting electrochemical cells.

**Results**

In direct comparisons between ITO-based and SWNT film-based LECs, it was found that though both devices achieved light emission, the ITO-based devices achieved nearly five times the luminance observed in SWNT-based devices with an improved current efficiency (in terms of luminance per current required) in the ITO based devices (Figure 6-3). One phenomenon that was observed but is not shown in the data is that many SWNT-based LECs that were initially non-shorted developed shorts after application of moderate to low voltages (often less than 4 V). A literature review prompted by this observation discovered that PEO is a key component in many SWNT surfactants including Triton-X-100, the material that we use in our SWNT suspensions \(^{176,177}\). This suggests that the PEO may be acting to lift loosely bound SWNTs from the surface and into the active region – which may explain the relatively high currents at low luminance in the SWNT-based devices. To avoid this, a pyrene-
Functionalized polyfluorene based polymer (Sticky PF) was used to coat the SWNT film by soaking in solution and appeared to reduce, but not eliminate the shorting issue, though no significant change in performance was observed\(^{47}\).

Another possible explanation for the diminished performance is that the nanotubes may induce preferential phase segregation in the active layer around the SWNT surface. Such phase segregation could alter the MEH-PPV / PEO ratio in this region and inhibit balanced charge transport as well as the formation of a highly doped region. Phase segregation, arising from the mixing behavior of the non-polar MEH-PPV with the polar PEO solid electrolyte, is an important factor in LECs and can be seen in both ITO and SWNT LECs via AFM at the top surface of this polymer film in Figure 6-3. The phase segregation seen here is not uncommon and can be controlled either through additives or the use of a crown ether based electrolyte in place of the PEO. How this phase segregation changes at the SWNT film surface is difficult to discover without generating cross-sectional slices of the device for TEM via etching by focused ion beam which is both expensive and challenging – and the heating induced in this process could also damage the polymer itself. Though the use of crown ether alternatives might have

![Figure 6-3. A) Luminance and B) Current density data for a single emissive SWNT and ITO-based LEC. C) Phase segregation observed in AFM imaging of the LEC surface.](image)
been interesting, they would involve starting over from scratch and, in light of other publications on both SWNT-based LECs and dual emissive LECs, these avenues were not pursued.

**Dual Emissive Light Emitting Electrochemical Cells**

**Experimental Methods**

Though the performance of ITO-based LECs exceeded observed the performance in devices using a thin SWNT film, the mechanical flexibility of SWNT films offered an opportunity to create a novel, dual emissive device that was not available using ITO. For this device, SWNT films were transferred to both glass and polyethylene terephthalate (PET) substrates with predeposited gold electrodes using a thin chromium adhesion layer. PET is a transparent flexible material (tradename: Mylar) that tolerates many chemical solvents and did not require any major modifications of the film transfer process. The PET was cut into rectangular strips that were longer and narrower than the glass substrates used so the substrates would not fully overlap, allowing contact to be made to the gold electrode / SWNT film.

Solutions were mixed as described for the single emissive devices. These solutions were spuncast onto the SWNT films on both PET and glass substrates, again increasing from dilute solutions to a more concentrated ones. Immediately after the final spin, while the solutions were still wet, the PET and glass were placed in contact and clamped between metal plates using hand-held spring clamps to supply the force. Samples were left in clamps overnight forming the structure shown in Figure 6-4.

Device yield upon removal from clamps was low and appeared dependent on how wet the solution coated substrates were at time of clamping. If the substrate was either too wet (including when the solution was dropcast immediately prior to clamping) or too
dry, the stack did not adhere; controlled exposure to solvent vapor also proved ineffective. By trial and error, successful dual emissive devices were fabricated, though their stability if torque or stressed was not very good. Electrical contact was made to the gold electrodes using alligator clips and voltage supplied by a Keithley 2400 Sourcemeter.

Figure 6-4. Device schematic of a dual-emissive LEC.

Results

The lack of stability in the adhesion of the substrates made the measurement of the dual emissive devices difficult. The devices were measured in air to avoid mishandling in the glovebox. Lifetimes were short (minutes) and devices appeared to locally burn out, possibly due to inhomogeneities in the polymer layers from clamping. The instability of the device made accurate quantitative measurements impossible; however a picture showing device operation is shown in Figure 6-5. The device is photographed against a mirror to show emission in both directions. Though clearly room for improvement exists in this device, it shows the potential for use of SWNT films in light emitting devices that emit light in both directions.
Figure 6-5. Dual emissive LEC in light (left) and dark with emission (right).
CHAPTER 7
CONCLUSIONS AND PATHS FORWARD

This dissertation has demonstrated organic electronic devices that take advantage of the special properties of SWNTs in addition to new purification technique that will enable further progress in SWNT-based organic electronic devices by allowing for thinner organic active layers to be used. The continuous flow centrifuge technique demonstrated in Chapter 2 not only offers high levels of purity but also the throughput of material on a scale that is appropriate for industrial application. Though further studies may fine-tune the parameters and optimize this process, the ability to purify on this large scale allows future students to spend less time focusing on small batch purification of SWNTs and more time studying the fundamental physics that this material makes possible.

Substantial progress was also made in understanding Schottky barrier modulation at the interface of low density of state materials and organic semiconductors but there is room for even more growth in our understanding. Projects are underway already within the Rinzler lab to pattern both graphene and metal electrodes and compare the VFET architecture in low DOS state metals such as graphene directly to those using high DOS materials with a comparable work function (such as Ag). Similarly, though the fundamentals of graphene-enabled VFETs have been demonstrated here, there is much still to be learned in the role that pore size, density and pore ordering plays. With further understanding, and the incorporation of still thinner layers as allowed by the planar graphene, the outlook for these G-VFETs is promising. This dissertation has also demonstrated the versatility in the CN-VFET by incorporating solution processable materials that achieved state-of-the-art performance and n-type C60-based VFETs.
This progress should enable the incorporation of the VFETs into new devices such as CMOS-like inverters – work that is already underway.

Three different light emitting devices were also demonstrated within this work. Though SWNT-based OLEDs and LECs still cannot exceed the performance of ITO, in conventional devices there is potential for their incorporation in novel designs such as flexible OLEDs or the dual emissive LEC. Further investigation into these devices may also yield important insight for future advancements in novel designs such as the vertical organic light emitting transistor that incorporates a CN-VFET with an organic light emitting diode.

Low density of states electrodes offer exciting possibilities for device designs that help to move organic electronics beyond being existing technologies. There is significant room for exciting growth in the field and perhaps this work offers some hints at the future paths that these materials make possible. I am excited to see what the future holds for organic electronics.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Evan Peter Donoghue was born on July 21st, 1984 in Amherst, Massachusetts, the youngest sibling to two older sisters. With a physicist for a father and a librarian for a mother, he quickly became enamored with science and was bestowed with a love of learning. Though he lived his entire childhood in Amherst, his father’s work took his family on vacation across the globe in conjunction with conferences and sabbaticals. As he watched his father working on his theoretical calculations while relaxing a beach in the south of France, Evan realized that a career in physics might be an enjoyable lifestyle. It was not until years later that he learned the catch: while theoretical physicists can bring their work to the beach, experimental physicists spend much of their day working in a windowless basement laboratory.

Graduating from high school in 2002, he followed in his father’s (and grandfather’s) footsteps to the University of Notre Dame where, after a year in aerospace engineering, he decided that his calling was in physics. Though his school year was often dominated by his efforts on the Notre Dame Rowing Team, he spent his summers doing research both at the University of Massachusetts and the Jefferson National Accelerator Facility through the College of William and Mary. These efforts resulted in three publications and the opportunity to present his work at the Conference on RF Superconducting Cavities.

After graduating with a Bachelor of Science in Physics from the University of Notre Dame in 2006, Evan was drawn to Andrew Rinzler’s laboratory at the University of Florida where he saw the opportunity to connect his passion for physics with real world applications. He began work in June of 2006, the summer before enrolling in his first year of studies, and was quickly integrated into projects in collaboration with John
Reynolds’ group in the Department of Chemistry and began to probe the effects of doping on thin films of carbon nanotubes. This work led to the efforts in organic electronics and carbon nanotube purification that are seen here. Upon graduation, he will join eMagin Corporation to further this pursuit and contribute to the development of OLED displays for wide ranging applications.