APPROACHES FOR ALIGNMENT AND PURIFICATION OF SINGLE WALLED CARBON
NANOTUBE THIN FILMS AND THEIR APPLICATION IN DEVICE ELECTRONICS

BY

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DISSERTATION

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ABSTRACT

Thin films that consist of dense horizontally aligned arrays of semiconducting single walled carbon nanotubes (SWNTs) represent one of the most promising materials for low cost, high performance electronic today. Over the years, a great deal of progress has been made towards this goal, however, to date, there are still key challenges associated with achieving films with the required density, degree of alignment and without the presence of metallic single walled carbon nanotubes.

Here, we present fundamental studies of well-established techniques for chemical vapor deposition growth of aligned arrays and present a model for understanding this alignment based on strong Van der Waals interactions between the SWNT and the substrate. This model is experimentally validated through detailed study of alignment a variety of crystalline surfaces of quartz. Furthermore, the study reveals that current limitations to growth density are not intrinsic to the mode of alignment suggesting the potential for dramatic improvements in growth density.

Additionally, we present a methodology for purifying these arrays based on selective, joule heating induced thermocapillary flow in thin organic layers deposited on the array that is localized to the metallic SWNTs and subsequent etching to yield their removal. We provide statistically significant demonstrations to prove the effectiveness and selectivity of this approach and study the underlying physics of joule induced thermocapillary flow, which is critical to the effectiveness. Finally, we illustrate the scalability of this approach.

Lastly, we present several demonstrations of electronic devices based on aligned arrays (both purified and unpurified) and detailed characterization of their performance.
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CHAPTER 1

INTRODUCTION

The focus of the doctoral research presented here is to develop methodologies to create thin films of single walled carbon nanotubes (SWNTs) with properties suitable for advanced electronic applications. The approach is to utilize well established film synthesis techniques associated with chemical vapor deposition (CVD) to yield well aligned high purity s-SWNT films for device electronics. The scope of this work ranges from fundamental studies of underlying mechanisms for film alignment, to the development of advance techniques for purification, to applications of these approaches for basic device demonstrations. Alignment and purity of electronic type in SWNT films are key challenges to the field, and the main focus of this work. This introduction will define these challenges, and discuss various approaches taken to overcome them along with their benefits and shortcomings.

1.1 SWNT General Properties

Over the past several decades, SWNTs have become a common topic of research in many fields owing to their outstanding properties and the unique physics surrounding their quasi-one dimensional (1D) structure\textsuperscript{1-6}. In particular, their electrical properties (high electronic mobility\textsuperscript{6-8} and potential for ballistic transport\textsuperscript{9}) make them interesting for applications related to digital\textsuperscript{10-12} and RF analog electronic\textsuperscript{13-15} devices. To this end, SWNTs have been proposed as potential replacements for Si as advances which follow Moore’s law become limited\textsuperscript{16,17}. Additionally, excellent mechanical properties\textsuperscript{18,19} and ultrathin configurations, make SWNTs promising for applications such as flexible electronics\textsuperscript{10,20}. Their low intrinsic capacitance\textsuperscript{21} and the ability to operate in regimes where quantum capacitance dominates electrostatic capacitance,
make them suitable for high performance, linear RF analog electronics based on SWNTs\textsuperscript{13,22,23} (Chapter 5). Work in this area has yielded many impressive demonstrations to date; however, these have been significantly limited by challenges to achieve high densities of well-ordered SWNTs with homogeneous properties.

Large variation in properties that exist within a population of SWNTs represents a significant challenge to practical applications. These variations are intrinsic and related to the structure of the specific SWNT. The structure of a SWNT can be thought of as a sheet of graphene cut along a chiral vector (defined by a pair (n,m) as a linear combination of unit vectors \(a_1\) and \(a_2\), \(C_h=na_1+ma_2\), Figure 1.1) and rolled on itself, creating as tube of sp\(^2\) hybridized carbon whose surface is defined by continuous pi bonding, such that the diameter and chirality of the SWNT are defined by the length \(d=C_h/\pi\) and direction of the vector, respectively\textsuperscript{5}. The practical result is that within any given population of SWNTs, individual SWNTs may have a wide range of properties. Most dramatically SWNTs can be metallic (m-SWNT), semiconducting (s-SWNT), or semi-metallic (sm-SWNT). In practice, there is little to no difference between m-SWNTs and sm-SWNTs. However, the presence of either in applications which require populations of high purity s-SWNTs can be catastrophic (many applications require high on/off ratios, \(>10^4\), such that population purity must be \(>99.9\%\))\textsuperscript{24}. Among a random population of SWNTs, roughly 1/3 are expected to be m-SWNTs and 2/3 s-SWNTs. Beyond this almost all other electronic properties have a strong dependence on diameter. Electronic band gap depends on diameter, electronic mobility increases linearly with diameter and contact resistance increases dramatically for small diameter SWNTs\textsuperscript{5,6,25}. The result is that small diameter SWNTs have larger well defined band gaps at the expense of device conductance. The presence of these variations in electronic type and properties provides limitations for most
device demonstration, requiring complex film or device geometries or postprocessing techniques, whose details will form the bulk of this introduction. Alternatively, many demonstrations of SWNT devices are based on small numbers of SWNTs such that homogeneity of electronic type could be achieved by chance. While these studies provide invaluable insights into the performance of SWNTs and factors affecting it, they are not practical given their small current outputs (nA). Practical demonstrations require large numbers of SWNTs operating in parallel. For this reason, thin sub-monolayer films of SWNTs represent the most promising route for SWNT electronics. However, the geometry of the SWNTs in the film, the technique for depositing the SWNTs, and post-deposition treatments all play significant roles in determining the properties of the resulting film.

1.2 SWNT Thin Films

Monolayer thin films of SWNTs represent the most ideal way create electronic materials that exploit the intrinsic properties of SWNTs and can be practically integrated into current device technologies. However the properties of the resulting films depend dramatically on the configuration and properties of the SWNTs in the film itself and, as a consequence, the manner in which the film is created.

Film geometry plays an important role. The simplest cases involve random networks of SWNTs. These are of significant technological interest because they can mask the effects inhomogeneity of electronic type based on the nature of percolative transport through many SWNTs\textsuperscript{26}. Here, electronic pathways consist of many SWNTs such that a pathway need only contain one s-SWNT to exhibit high on/off ratio. When average path lengths become long, pathways naturally incorporate enough SWNTs to yield films with high on/off ratio, despite the
presence of m-SWNTs. However, the SWNT-SWNT junctions\textsuperscript{27} associated with these long percolative pathways typically result in films with reduced performance relative to the intrinsic performance of SWNTs. As a result, these films are promising for applications that do not require films with intrinsic properties (especially electronic mobility) equivalent to SWNTs themselves, such as flexible electronics\textsuperscript{10,11}. Furthermore, these types of geometries are not consistent with short channel devices, where percolation effects are minimized.

Most advanced applications require improved properties, closer to those of individual SWNTs. Films of SWNTs in perfectly aligned horizontal arrays provide this\textsuperscript{7,28}. Chapters 1.3 and 2 focus on various approaches to achieve alignment in SWNT films. Regardless of the geometry, factors such as average SWNT length and SWNT density play a critical role. In random configurations, the effects of length and density can be complex\textsuperscript{26}, but for aligned arrays the effects are straightforward: Average SWNT length will dictate the maximum distance films can span and the SWNT density will determine the overall conductance of the film (relative to the constituent SWNTs)\textsuperscript{29}.

Beyond factors associated with film geometry, the population of SWNTs that make up the film play a critical role. Electronic purity is critically important\textsuperscript{24}. Chapters 1.4, 3, and 4 focus on approaches to achieve this. More subtle effects can result from the diameter distribution of the SWNTs that make up the film, which lead to variations in mobility, contact resistance and other properties among the SWNT that make up the film\textsuperscript{30}. Finally, the cleanliness and quality of the SWNTs in the final film are important. Many intrinsic properties can be degraded by bound surface molecules or introduction of defect into the structure of the SWNT\textsuperscript{31}. For certain processes, this can play a significant role.
1.2.1 Solution Deposition of SWNT films

One class of techniques for creating films of SWNTs involves suspending large quantities of SWNTs (via bulk synthesis) in solution, depositing them onto a substrate\textsuperscript{32-34}. Most of these techniques are attractive because they are scalable, cost effective, and compatible with a wide range of substrates. The basic approach requires creation of a stable suspension of SWNTs. This is typically achieved via some form of surfactant. Today, such solutions of SWNTs can be purchased commercially. Critical attributes of these solutions are related to the synthesis technique for the bulk SWNTs, which dictates the diameter distribution and allows some control of the electronic purity of the resulting SWNT population (as in the case of CoCatMo based synthesis\textsuperscript{35}). Chemical treatments can be applied in solution to further modify these populations (see Chapter 1.4.1). Once solutions are created, an appropriate technique must be utilized to deposit SWNTs on the substrate from solution. This is typically accomplished through evaporation of the solvent, chemical interactions, or interaction between SWNTs and the substrate itself\textsuperscript{32,33,36}. Basic approaches such as vacuum filtration involve flow of solvents through a filter resulting in accumulations of a film\textsuperscript{36}. These approaches, however, yield very poor control over the resulting film density or geometry. More advanced techniques such as controlled flocculation (cF) utilize miscible liquids which destabilize suspended SWNTs to facilitate their deposition onto substrates and can provide greater control of the resulting film\textsuperscript{37}. Regardless of the process, the ability to apply forces to the SWNT themselves during deposition is the key to achieving highly ordered films (Chapter 1.3.1). While the details of the SWNT source, solution, surfactant and deposition technique are important, all approaches to solution deposition of SWNTs utilize steps such as acid purification or ultrasonication to achieve
suspended solution, resulting in shorter average SWNT length, with a many surface bound molecules that can be difficult to remove and result in a general reduction of key properties (intrinsic SWNT mobilities of ~200-300 cm²/V/s, much lower than those associated with other growth techniques, 1,000-3,000 cm²/V/s).\textsuperscript{7,38}

1.2.2 Chemical Vapor Deposition

Given the proper, catalyst, growth condition and gas flow, SWNT films can be directly grown by chemical vapor deposition (CVD).\textsuperscript{39,40} Here, catalyst particles, typically metal nanoparticles (most commonly Fe or Cu) with diameters comparable to the SWNT diameter are deposited on the substrate prior to growth. These substrates are heated in a CVD reactor in the presence of a carbon feedstock gas (typically, methane, ethanol vapor, or ethylene, often mixed with an inert gas such as Ar or H\textsubscript{2}) yielding direct growth of SWNT films. Optimization of gas flow rates, gas composition, and growth temperature can yield excellent control of the growth (density, growth rate, average length). Furthermore, application of external forces (via gas flow, substrate interaction, electrostatically or other) during growth can yield alignment (Chapter 1.3.2). Relative to solution deposited films, those grown by CVD offer better control of alignment, longer SWNTs, and cleaner SWNTs with better electronic properties.\textsuperscript{7} However, achieving films with the required electronic purity for advanced applications remains a significant challenge. Because of these advantages, the research presented here focuses exclusively on SWNT films grown by CVD.

1.3 Alignment and Density of SWNT films

For the reasons described above, achieving films that consist of horizontally aligned arrays of SWNTs is of critical importance for advanced applications. Critical factors are the
degree of alignment (magnitude of deviation from the average alignment direction), frequency of misalignment, and the maximum achievable density. Related to these factors, it is important that the resulting films minimize overlapping SWNTs and bundles.

1.3.1 Alignment from Solution

Alignment from solutions has been achieved in a wide variety of ways. Almost all of them rely on the application of forces on the SWNTs during deposition onto substrates. One approach utilizes the applications of fluid forces during cF\textsuperscript{37}. While these approaches are fairly straightforward, the degree of alignment and density is relatively poor, as seen in Figure 1.2d. Other approaches utilize electronic or magnetic fields to attract SWNTs to the substrate and simultaneously yield alignment\textsuperscript{41,42}. These approaches can yield very high densities with fairly high degrees of alignment. In the case of AC dielectrophoresis, m-SWNTs are preferentially deposited due to enhanced dipole moments associated with their dielectric constant\textsuperscript{41}. These approaches are fairly effective; however the need for prepatterned electrodes and electrical contact during deposition can be cumbersome. Figure 1.2e shows the resulting film. Alternatively, interfacial solution forces can be utilized to facilitate alignment as is the case for Langmuir-Blodgett (L-B) techniques\textsuperscript{43}, which yield higher density and good alignment. These techniques yield fairly high densities (not always well characterized, but estimation from published images suggests \(~40\)-\(50\) SWNT/\(\mu\)m), however their drawbacks are the degree of alignment and other general issues with SWNT quality associated with solution based approaches.

1.3.2 Alignment from CVD
Similar to solution approaches, the key to alignment in CVD grown SWNT films is the application of appropriate forces during growth itself. One simple way to achieve this is via the gas flow of the carbon feedstock gas. Here optimized flow conditions yield alignment via eddy currents associated with very low flow rates (~1 sccm) or the forces associated with high flow rates (>100 sccm)\textsuperscript{44,45}. This approach is straightforward and it can yield extremely long SWNTs (cm), however it allows for only moderate alignment and very low densities (Figure 1.2b).

Alternatively, electric fields applied during growth can yield alignments, however the degree of alignment and density is similar to flow based techniques and is, practically speaking, more difficult (Figure 1.2a)\textsuperscript{46}. The most promising approach involves alignment during growth with the underlying crystalline substrate. The best examples of this are sapphire and quartz\textsuperscript{7,28,47,48}. For ST cut quartz, long (100’s of μm), high density (~10 SWNTs/μm), aligned arrays can be grown where >99.9% of the SWNTs are aligned within 0.01° of the growth direction (Figure 1.2c, the white regions are dense unaligned regions where catalyst particle are lithographically isolated, the aligned SWNTs can be seen bridging these regions). This is perhaps the most effective mode of SWNTs alignment. Chapter 2 describes fundamental studies which elucidate the underlying mechanisms associated with this type of aligned growth. Finally, it is important to note that the placement of catalyst particles plays a practical role in the alignment, resulting in early termination of SWNTs and contributing significant misalignment in arrays. For optimal results, high densities of catalyst are confined to discrete regions (lithographically). In these regions, SWNTs form thick randomly aligned layers (>1 monolayer) due to the high density of SWNTs locally, however a small percentage grow out of these regions, align with the substrate, and extend across the open region of the substrate. By comparison to solution based approaches, CVD approaches can achieve much higher degrees of alignment, with better intrinsic electronic
properties. The key drawbacks are related to SWNT density and challenges associated with achieving electrically pure films (Chapter 1.4.2).

1.4 Purification of SWNT Films

As discussed above, many applications of SWNTs require high purity populations with homogeneous electronic type (for the applications here, typically s-SWNT populations are desirable). It is important to consider what degree of purity is required for applications when choosing an approach. For example, most digital electronics require high on/off ratio (>10^3-10^4), necessitating >99.9% pure populations, while RF analog devices, can tolerate lower on/off (10-100). Furthermore, when considering purification scheme, it is important that they also be cost effective, scalable, and not significantly degrade the properties of the SWNTs themselves. The application requirements, effectiveness of the approach, and all of these factors should be considered when evaluating purification techniques. To date, all purification approaches are insufficient in one or several of these areas for many applications. Chapters 3 and 4 discuss details of an alternative approach which is highly effective, scalable, and does not degrade SWNT properties.

1.4.1 Solution Purification

Perhaps the greatest advantage of depositing SWNT films from solution are the wide variety of techniques that allow for purification using selective chemistries which bind to different SWNT types with varying affinity, yielding differences in density that can be exploited by physical purification techniques such as ultracentrifugation or chromatography\(^{49-51}\). Figure 1.3a shows a solution of SWNTs following density gradient ultracentrifugation. Clear bands with unique optical absorbance represent separated populations of SWNTs. A wide variety of
chemistries have been exploited to allow sorting based on diameter or other factors, however, only a few chemistries have allowed for selective sorting by electronic type. These include flourene based polymer wrapping\(^5\), DNA wrapping\(^6\), and competitive surface interactions between co-surfactant mixtures \(^7\). These approaches can yield solutions with up to 99\% pure s-SWNT populations and in some cases have been shown to select for chirality. Furthermore, they are scalable and depending on the technique can be fairly cost effective. The key drawbacks of all of these approaches are the challenges to align and achieve optimal electronic properties.

1.4.2 Post-deposition Purification

A second class of purification approaches attempt to selectively degrade as deposited (or as grown) films of SWNTs on the substrate. These approaches are compatible with CVD approaches which offer direct growth of well aligned SWNTs with superior properties, however, they are generally highly ineffective. A wide variety of approaches (chemical\(^5\)-\(^7\), optical\(^8\), electrical\(^9\), or other\(^10\); several are illustrated in Figure 1.3b,c,d) have been shown to damage SWNTs with some preference for m-SWNTs, however almost all either leave a significant percentage of m-SWNTs, destroy or degrade a significant percentage of s-SWNTs or both. Many are subject to very strong diameter dependencies, showing some selectivity for a small range of diameters, but destroying all SWNTs above that range, and preserving all below it. The outcome is that almost none of these can be applied to typical populations of SWNTs and yield high purity populations of s-SWNTs without significant degradation to the preserved population. One partial, but notable exception is electrical breakdown\(^9\), whereby, SWNTs are built in transistor configurations, and significant levels of current are applied to m-SWNTs, while current flow is minimized in s-SWNTs via a capacitively coupled gate electrode. Current flow is increased to the point where Joule heating induces electrical breakdown in the m-SWNTs,
leaving only s-SWNTs. However, the high power required to yield electrical breakdown leads to a variety of undesirable effects such as threshold voltage shift, avalanche effects, band to band tunneling and dielectric breakdown, which either lead to damage to the device architecture or the s-SWNTs themselves. Finally, this approach does not remove SWNTs entirely, but instead removes a narrow portion of the SWNTs such that a majority of the m-SWNTs remain. This requires that final devices be consistent with the electrode geometry used for breakdown, which does not provide a scalable approach for purification. This is illustrated schematically in Figure 1.4. Here, large area electrodes are applied to perform selective removal on an array, removed, and new high performance devices are built on the treated SWNTs. Only the arrays that yield full physical removal avoid reincorporating m-SWNTs. Chapters 3 and 4 outline approaches for purification which achieve the type of complete physical removal envisioned here and as a result are compatible with such scaled approaches for purification.

1.5 In this Thesis

Chapter 1 provides a general overview of the current state of the art for creating aligned purified films of SWNTs.

Chapter 2 describes a study that combines detailed modeling and rigorous experimental characterization of SWNT growth on single crystalline quartz substrates in order to elucidate key details about the underlying mechanism for and various practical aspects of this type of aligned SWNT growth based on substrate interaction. Theoretical and practical aspects of substrate choice, surface quality, and SWNT diameter on the quality of alignment are discussed.

Chapter 3 describes a technique for purifying aligned arrays of SWNT termed thermocapillary enhanced purifications (TcEP), whereby local joule induced thermocapillary flow
(Tc-flow) in the vicinity of m-SWNTs is used to pattern thin layers of resist material and subsequent etching yields complete physical removal of these SWNTs from arrays. Proof of concept studies on small arrays of SWNT that are characterized in detail throughout the process provide clear evidence that TcEP is provides highly selective removal (removing all m-SWNTs, preserving most or all s-SWNTs) and yields complete physical removal of m-SWNTs. The detailed theoretical and experimental study of thermal and thermocapillary aspects of Tc-flow are explored, revealing key features which are critical to the effectiveness of TcEP. Finally, scalability is demonstrated. Approaches to treat large arrays with hundreds or thousands of SWNTs in parallel manners are shown.

Chapter 4 describes the more detailed aspects of TcEP. Studies utilizing TcEP on individual SWNTs (or several SWNTs) devices provide insight about the process itself, ideal configurations for electrode geometries and optimized conditions. Analytical modeling and detailed experimental study of the time dependence of Tc-flow provide insight into the process and various critical aspects of it. Materials selection is discussed, both experimentally and theoretically. Key features of effective thermocapillary resist (Tc-resist) materials are identified.

Chapter 5 describes a variety of device demonstrations based aligned arrays of SWNTs. Fabrication and study of RF analog transistors with sub-micron channel lengths are based on unpurified arrays are described. Scaling studies and device modeling reveals the role of device parasitics and m-SWNTs within arrays, identifying potential for improvement and fundamental limitations within devices. Fabrication and study of basic transistors using arrays processed by TcEP shows the utility of the process.
Chapter 6 provides an overview of the research presented here and a discussion of directions for future work.

1.6 References


1.7 Figures

Figure 1.1 Typical carbon nanotube structures. a, Schematic representations of a single-walled carbon nanotube (SWNT), a multiwalled carbon nanotube (MWNT) and a bundle of SWNTs. b, Conceptually, a SWNT is formed by rolling up graphene along a chiral vector to form a cylinder. The circumference of the SWNT is determined by its chiral vector $C = na_1 + ma_2$, where $(n,m)$ are integers known as the chiral indices and $a_1$ and $a_2$ are the unit vectors of the graphene lattice. Nanotubes with $n = m$ (known as armchair nanotubes) and those with $n - m = 3j$, where $j = 0,1,2,3,\ldots$, are metallic at room temperature (labelled green). Carbon nanotubes with $n - m = 3j + 1$ (labelled pink) and $n - m = 3j + 2$ (labelled purple) are semiconductors with a bandgap that varies inversely with diameter. Nanotubes with $m = 0$ are known as zigzag nanotubes and can be either metallic or semiconducting. $\theta$ is the chiral angle. c, Schematic representation of two SWNTs with nearly identical diameters but different chiral indices. d, Schematic representation of two SWNTs with identical chiral vectors but different chiral handedness.

Reproduced from reference 49.
Figure 1.2. Forms of alignment in SWNT films. Demonstrations of various approaches for achieving SWNT alignment.

(a,b,c) Alignment during CVD growth of SWNT achieved by applications of electric field (a), and control of gas flow (b), interactions with quartz substrate (c). (d,e) Alignment during depositions of SWNT onto substrates from solution via controlled flocculation and solution flow (d) and AC dielectrophoresis (e). Reproduced from references 7, 37, 41, 44, and 46.
Figure 1.3 Various approaches for SWNT purification. (a) Solution of suspended SWNT following density gradient ultracentrifugation. Clear bands with distinct optical absorbance can be observed associated with layers containing different populations of SWNTs. (b,c) Electrical characteristics of SWNT transistors before and after treatment with methane plasma (b) and diazonium salt (c). In both cases there is a dramatic decrease in conduction consistent with destruction of or damage to some s-SWNT. (d) Schematic illustration of approach for selective destruction via optical exposure. Reproduced from references 50, 57, 58 and 60.
Figure 1.4 Schematic illustration of requirements for scalable purification. Schematic illustration of the drawbacks to purification via electrical breakdown. Here the envisioned approach is to treat large areas of SWNT via electrical breakdown remove the electrodes used for large area treatment and build new high performance circuits or devices on the purified arrays. However, because SWNT were not completely removed, they are reincorporated into the devices. Alternatively, a similar approach that yields complete physical removal is compatible with this type of approach.
CHAPTER 2

ALIGNMENT STUDIES ON SINGLE CRYSTALLINE QUARTZ SUBSTRATES

Significant portions this chapter were published as “Alignment Controlled Growth of Single-Walled Carbon Nanotubes on Quartz Substrates,” J. Xiao, S. Dunham, P. Liu, Y. Zhang, C. Kocabas, L. Moh, Y. Huang, K.-C. Hwang, C. Lu, W. Huang, and J.A. Rogers, Nano Letters, 9 (12), 4311, (2009). Reproduced with permission from the journal. This work was highly collaborative, however, I was not involved in the analytical derivations presented in this work. That content is included because it provides critical context to the experiments and analysis discussed here.

2.1 Introduction

The attractive charge transport properties of single-walled carbon nanotubes (SWNTs) make them excellent candidates for various applications in electronics, ranging from radio frequency (rf) analog devices\textsuperscript{1-4}, to flexible circuits\textsuperscript{5}, to heterogeneous integration of such systems with silicon complementary oxide semiconductor (CMOS) chips\textsuperscript{6}. Large scale, horizontally aligned arrays of SWNTs represent ideal formats for integration, with the demonstrated ability to yield devices with performance approaching expectation based on the intrinsic properties of the constituent SWNTs\textsuperscript{1,2}. Many different methods have been reported to produce such arrays. Flow alignment is one of the most widely explored strategies, implemented either during deposition from solution via the action of liquid flows\textsuperscript{5} or during chemical vapor deposition (CVD) via gas flows\textsuperscript{8,9}. In the case of solution deposition, surface chemical modifications of the substrate can provide additional levels of control\textsuperscript{10}. Electric fields, applied in an alternating current mode during solution deposition\textsuperscript{11} or in a direct current mode during
CVD growth\textsuperscript{12} can also yield alignment, due to dielectrophoretic and induced dipole interactions, respectively. Although each of these methods has promise, none in their current state of development offers the levels of perfection in alignment and linearity, at densities (i.e., numbers of tubes per unit area) and average lengths useful for most applications in electronics. More recent work\textsuperscript{13,14} indicates that improvements can be achieved by using wetting interactions and interface assembly to yield high density (10-20 SWNTs/\textmu{m}) arrays with good, although not perfect, degrees of alignment. The use of SWNTs in solution suspension could represent a disadvantage, however, due to possible contamination by residual surfactant and the potential for degradation of the tubes during the solubilization process. By contrast, growth of SWNTs by CVD on crystalline substrates such as sapphire and quartz can produce nearly ideal arrangements of low-defect tubes, particularly when used with strategically patterned catalyst particles\textsuperscript{15-23}. The best results have been reported on quartz, where levels of alignment can be controlled to better than 0.01°, with linear shapes to within a few nanometers over lengths of many micrometers, in tubes with average lengths of hundreds of micrometers (up to \(\sim\) millimeters)\textsuperscript{4,16-23}. Densities can also be high, with peak values approaching 100 SWNTs/\textmu{m}\textsuperscript{17}. Although this growth process has already been exploited to build high-performance n and p channel devices\textsuperscript{3,15,20,21}, and even fully integrated systems such as nanotube transistor radios and oscillators\textsuperscript{1,2}, the underlying mechanisms are poorly understood and the achieved alignment in the arrays involve orientation only along one direction. This paper presents a comprehensive, combined theoretical and experimental study of the alignment process on quartz and presents strategies to use quartz with different crystal orientations to achieve not only aligned linear arrays, but also more complex, but still well-defined, layouts. The results account for the key aspects, ranging from previously reported trends to additional effects revealed by new results.
reported here. This basic understanding is essential for further development of this approach to
aligned arrays or even to other arrangements, not only on quartz but, potentially, on crystalline
substrates of other materials.

2.2 Molecular Model for Alignment of SWNTs on Crystalline Substrates

Figure 2.1 provides a schematic illustration of the modeled system. We consider four
cases—quartz with X ([2̅1̅0̅]), Y ([01̅0̅]), Z ([0001]), and ST cut orientations—to examine all
of the effects of crystal orientation on alignment. α-Quartz is used in this study, since the
transition between α- and β-quartz is very fast and highly reversible at 573 °C24,25 and the
experimental observations are all made at room temperature. Tridymite may also form at 870 °C,
since the SWNT growth temperature is 925 °C. However, previous studies show that the
transition from quartz to tridymite requires foreign oxides and the transition rate is very slow
even when they are well mixed26. Under the experimental conditions of SWNT growth as
described in the methods section, no or only a very negligible amount of tridymite should form.
In any case, calculations for α- and β-quartz give the same preferred alignment directions. In
addition to proper atomic descriptions of the substrate, we treat the SWNTs explicitly with
suitable chiral and diameter dependent configurations of the carbon atoms. Several experimental
observations suggest the validity of important simplifying assumptions for the modeling. First, in
all cases, the SWNTs grown on Y or ST cut quartz show excellent degrees of alignment,
uniformly and without any evident dependence on chirality or diameter, for values smaller than
∼1.5 nm. This observation suggests that neither epitaxial registration with the substrate nor
electronic properties of the SWNTs are critically important. Second, insensitivity of growth
results to location or orientation of the quartz within the furnace or to spatial position across the
substrate are consistent with uniform temperature distributions and, as a result, the absence of
significant pyroelectric effects. Third, observations of alignment in SWNTs that fall back onto the substrate after growth in gas flows just above the substrate surface\textsuperscript{17,27,28} indicate that interactions between catalyst particles and the substrate can be neglected. Aligned SWNTs at spacings (minimum, as well as averages) that are smaller than the expected separations between adjacent step edges based on slight uncertainties in the cut angle (Y cut) suggest that steps are unimportant. In addition, in certain experiments, SWNTs align in directions roughly perpendicular to clearly observable step edges, as described subsequently. Collectively, these observations suggest that it might be possible to treat the system with a simple model in which the alignment of SWNTs is governed by angle-dependent van der Waals (vdW) interactions, provided there is no significant permanent charge on the tubes or the quartz. (Polarization and piezoelectric effects do not require net charge and can contribute to the interaction energy but they do not change the alignment preference, as discussed subsequently).

Using this view of the essential physics, we begin with molecular mechanics simulations based on empirical interatomic potentials\textsuperscript{29,30} to obtain the vdW interaction energies for (5, 5) armchair and (9, 0) zigzag SWNTs sitting on Y cut quartz, as shown in Figure 2a by blue and red dots, respectively. The orientation angle $\theta$ of the SWNT is measured from the $x$ direction ([2110]). The energy for $\theta = 0$ is taken as zero as a reference state. The quartz surface is obtained by cutting between two oxygen layers, saturating the terminal oxygen atoms on the surface with hydrogen atoms and then reconstructing by ReaxFF (reactive force field) method, which can accurately simulate bond breaking and formation in silicon oxide systems\textsuperscript{31}. The obtained quartz surface structure is consistent with previous experimental\textsuperscript{32} and first principles dynamics studies\textsuperscript{33-36}. The SWNTs are sufficiently long such that the influence of local epitaxial registration is negligible. Figure 2.2a shows that both armchair and zigzag SWNTs have global
energy minima at 0° (x direction), and local energy minima at ±48° and ±90° (z direction). The results indicate that SWNTs with similar diameter but different chiralities have negligible differences in their interaction energies with the substrate. Molecular dynamics simulations confirm that SWNTs aligned along the 0° direction are stable at the growth temperature (∼1200 K).

These results suggest the applicability of a simple analytical model to represent the vdW interactions, in which the SWNT is treated as a continuous cylinder. These interactions can be represented by the Lennard-Jones potential

$$V(r) = 4\varepsilon \left( \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right)$$

where $r$ is the distance between two atoms, $\sigma = 0.3621$ nm and $\varepsilon = 6.46 \times 10^{-3}$ eV for C-Si interaction, $\sigma = 0.3340$ nm and $\varepsilon = 3.86 \times 10^{-3}$ eV for C-O interaction, and $\sigma = 0.3110$ nm and $\varepsilon = 1.33 \times 10^{-3}$ eV for C-H interaction. For a long SWNT of radius $R$ sitting on top of the quartz surface, as shown in Figure 2.1, the vdW interaction between each atom in the substrate and the entire SWNT is the sum of $V(r)$ over all carbon atoms, which can be accurately represented by integration over the SWNT surface

$$\phi = \int_{\text{SWNT surface}} V(r) p dS$$

where $p = 38.2$ nm$^{-2}$ is the carbon atom density on the SWNT surface. For an atom in the substrate with a distance $\zeta$ to the SWNT axis, the above integration is obtained analytically as

$$\phi = 4\varepsilon p R \left( \sigma^{12} g_{12} - \sigma^6 g_6 \right),$$
where \( g_6 = \frac{\pi}{2(\zeta + R)^2(\zeta - R)^2} \left[ 4(\zeta^2 + R^2) E \left( \frac{2\sqrt{\zeta R}}{\zeta + R} \right) - (\zeta - R)^2 K \left( \frac{2\sqrt{\zeta R}}{\zeta + R} \right) \right], \)

\[
g_{12} = \frac{\left( \zeta^2 + R^2 \right) \left( 31\zeta^4 + 194\zeta^2 R^2 + 31R^4 \right)}{20 \left( \zeta^2 - R^2 \right)^6} g_6 - \frac{3\pi \left( 143\zeta^4 + 482\zeta^2 R^2 + 143 R^4 \right)}{320 \left( \zeta + R \right)^7 \left( \zeta - R \right)^8} E \left( \frac{2\sqrt{\zeta R}}{\zeta + R} \right), \text{ and} \]

\[
K(k) = \int_0^\pi \frac{1}{\sqrt{1 - k^2 \sin^2 t}} dt \text{ and } E(k) = \int_0^\pi \sqrt{1 - k^2 \sin^2 t} dt
\]

are complete elliptic integrals of the first and second kind, respectively. The sum of \( \varphi \) for all the silicon, oxygen, and hydrogen atoms in the substrate gives the total van der Waals energy, which depends on the SWNT orientation \( \theta \), distance \( h \) between the SWNT axis and the substrate surface, and the shift \( \eta \) along the substrate, normal to the long axis of the SWNT. For each given orientation \( \theta \), minimization of the total energy with respect to \( h \) and \( \eta \) gives an “energy map”, as shown in Figure 2.2a by a black curve for the Y cut case, where \( \theta \) is measured from the \( x \) direction, and the energy for \( \theta = 0 \) is taken as zero, as for the molecular mechanics modeling.

The long SWNT of Figure 2.2a has a radius of 0.35 nm, close to that of (5, 5) armchair and (9, 0) zigzag SWNTs. The size of the quartz substrate was 20 \( \times \) 20 nm; convergence was verified by comparing the results with substrates of size 40 \( \times \) 40 nm. As shown in Figure 2.2a, the results given by this relatively simple analytical model agree well with the full molecular mechanics simulation, and predict a global energy minimum at 0° (\( x \) direction), and local minima at \( \pm 48^\circ \) and \( \pm 90^\circ \) (\( z \) direction). Similar calculations performed on SWNTs with \( R \) in the range typically observed from CVD deposition appear in Figure 2.2b, clearly showing energy minima at 0° for SWNTs with \( R \) equal to 0.35, 0.6, 1.2, and 2 nm. The depth of these energy wells decreases with increasing \( R \).
The energetically favorable orientations, as illustrated by green dashed lines in Figure 2.1a, can be interpreted in terms of the atomic structure of the quartz. In Figure 2.1a, the top layer of silicon atoms, which are marked by black triangles, form a rectangular lattice. These silicon atoms also form parallel arrays when viewed along different directions. The 0° (x direction) orientation gives the largest spacing between adjacent arrays of silicon atoms, 0.54 nm as shown in Figure 2.1a. This configuration allows the SWNTs to interact most effectively with quartz and hence gives the global energy minimum, consistent with a global minimum in h at this same orientation. See Figure 2.2c. The local minima at ±48° and ±90° (z direction) can also be similarly explained since they correspond to the next two largest spacing between adjacent arrays of silicon atoms, 0.36 and 0.49 nm as shown in Figure 2.1a. Further insight into the underlying physics can be obtained by approximating the interaction between the tubes and the quartz as purely hard spheres (i.e., by taking limiting cases of the Lennard-Jones potential in which σ for C-Si, C-O, and C-H interactions are 1/10 of the original values as given previously). Even this highly simplified analysis, shown in Figure 2.2d, captures the global and local minima in energy and h along 0°. These results suggest that the surface interactions are dominant, and that one can intuitively consider the alignment as due to oriented “trenches” on the quartz with depths of ~0.1 nm. As R increases, the significance of these trenches decreases, thereby reducing the depth of the energy well and the degree of alignment.

These trends are consistent with experimental observations of growth of SWNTs by CVD. (See the methods section for growth conditions.) Figure 2.3 shows some results. The SWNTs have a range of chiralities, with a diameter distribution illustrated by the histogram in the inset of Figure 2.3a. (This distribution is indistinguishable from that obtained in random networks of SWNTs grown on amorphous thermal oxides on silicon wafers using conditions and
catalysts that are otherwise similar.) The primary alignment is along the $x$ direction, but on rare occasions ($\sim$0.1-4%, depending on the sample) segments of SWNTs can be observed in well-defined off-axis orientations of $45 \pm 5^\circ$, as highlighted by circles in Figure 2.3b. The inset shows a histogram of the frequency of aligned segments versus angle, weighted by segment length, ignoring segments very close to the catalyst regions or those that show no strong alignment (most likely due to turbulent gas flow). In rare cases (<0.1%) misaligned SWNTs at angles near $90^\circ$ were observed. We suspect that the rarity of SWNT segments at $90^\circ$ ($z$ direction) is due to a shallower energy well compared to $0$ or $45^\circ$. Furthermore, bending of a SWNT initially growing along $0^\circ$ toward $90^\circ$ requires higher energy compared to bending toward $45^\circ$.

The orange arrow indicates the direction of gas flow. While it coincides with the alignment direction, the same characteristic behavior was observed for various flow directions. The same is true for all crystal orientations discussed subsequently indicating that gas flow does not play a major role in the observed alignment. Figure 2.3c shows the effect of diameter on alignment for $>60$ SWNTs measured by atomic force microscopy (AFM). For nanotubes less than 0.8 nm in diameter, almost no misalignment was observed over the $10 \times 10 \mu m$ scan they were observed over, while almost all nanotubes above 1.2 nm in diameter demonstrated some degree of misalignment. In the intermediate diameter range, varying degrees of alignment were observed. All of these observations are consistent with the modeling results presented in Figure 2.2.

Although this level of agreement is encouraging, one drawback of the model is that it assumes an atomically smooth surface, whereas the actual substrates have root mean squared roughness in the range of 0.2-0.4 nm as measured by AFM with conventional tips, and in some cases step edges can be observed. Effects of finite roughness can be examined theoretically by considering the case of a SWNT that encounters a feature of relief as it is growing on the surface.
The tube can either climb over this feature or turn to grow along it, depending on which gives the lower energy\textsuperscript{46}. The critical height of a feature (Figure 4a) below which a SWNT of radius $R$ can climb over can be shown to be

$$h < \frac{3\pi (\pi - 2)}{128} \sqrt{\frac{E\tau R^3}{2\gamma_0}}$$

(4)

where $E\tau = 0.42$ TPa·nm is the tension rigidity of SWNT\textsuperscript{47,48}, $\gamma_0$ is the adhesion energy between SWNT and quartz, and $\gamma_0 = 1.79$ eV/nm for $R = 0.6$ nm. This result, which is based purely on mechanics and ignores potentially important effects associated with the growth process, suggests that a SWNT of radius 0.6 nm can climb over any feature with height less than 1.88 nm.

According to this analysis, surface roughness of standard quartz wafers used here should not impede aligned growth. To demonstrate explicitly the relative insensitivity to moderate surface roughness and to provide information on the possible role of step edges, we grew tubes on $Y$ cut wafers with a miscut of $\sim 0.1^\circ$, to create organized steps with relief heights of $\sim 0.4$ nm oriented approximately about 20° from the $z$-direction ($\theta = 70^\circ$). Experimentally, we observed the expected tube alignment, even though the direction is almost orthogonal to the step edges, as shown in Figure 2.4a. The overall alignment is somewhat worse than that on smoother, polished substrates used for the results of Figure 2.2. Previous publications indicate an ability to grow over sharp edges of relief with heights of $\sim 1$-2 nm, but not much more\textsuperscript{17,18}. Additionally, random surface roughness can contribute to lower degrees of alignment, although such systems are less well amenable to modeling due to the range of lateral length scales involved in the relief.
In order to study the effect of roughness on orientation, Y-cut quartz samples were polished using 0.1 – 1 μm grit diamond polishing papers in order to generate substrates with roughness ranging from 0.1 to 1.5 nm RMS. Figure 2.7 shows an AFM of a sample with an RMS roughness of ~0.2 nm. For very smooth samples (<0.3 nm RMS roughness) step edges were observed to start to form during growth itself, however are not well defined enough to have a substantial effect on the overall alignment (as compare to well defined steps in Figure 4). This can be seen in Figure 2.7 clearly. Figure 2.8 shows SEM images of various substrates polished to varying degrees of roughness. For all substrates the overall alignment is still fairly strong and for those less than 0.8 nm RMS roughness it is extremely strong. Figure 2.9 shows AFM of a substrate with 0.85 nm RMS roughness that still shows extremely strong alignment. In fact, the sample is so rough that the SWNT cannot be observed in the topography image. Here Dual Frequency AFM was used to provide the contrast needed to observe SWNT, whose alignment is nearly perfect. For Dual frequency AFM the drive signal for the cantilever was the sum of a signal at the resonant frequency (~75 kHz) and another with ~1% of the amplitude of the primary signal at 6 times the primary resonant frequency. The contrast is seen in the amplitude of the higher frequency signal. Figure 2.9a shows the primary amplitude height signal which is identical to the height image taken with standard single frequency imaging. Figure 2.9b shows the amplitude signal from the higher frequency.

These observations clearly demonstrate that aligned tubes can form without and, in fact, despite the presence of steps. They do not, however, rule out the possibility that steps could give rise to alignment in certain situations. Additional analysis can provide some insights. Figure 2.4b shows the vdW energy of a SWNT of radius 0.35 nm adjacent to a step edge of height 0.43 nm for Y cut quartz. The SWNT and the step edge are along the x direction, the preferred growth
direction, and \( z = 0 \) denotes the SWNT axis being on top of the step edge. The step edge clearly reduces the energy minimum, which is 0.11 eV/nm lower than the minimal energy away from the edge. This effect is, however, localized: the energy minimum occurs at 0.82 nm from the step edge, but drops to negligible values at distances of more than \( \sim 1.1 \) nm. A (5,5) armchair SWNT that is initially 1.0 nm from the step edge but forms a 5° angle moves toward and becomes parallel to the step. For the same angle but at an average distance of 1.8 nm, the SWNT aligns along the \( x \) direction but does not move toward the step. For a typical commercially available Y cut substrate, the miscut angle is \(<0.25°\). This angle corresponds to an average separation between steps of \( \sim 100 \) nm, assuming step heights of \( \sim 0.4 \) nm. This distance is much larger than separations that are often observed between adjacent SWNTs in arrays grown on Y cut substrates. Collectively, these results rule out step edges as a major cause of alignment.

Although these observations and calculations indicate some insensitivity to surface topology due to steps or to random roughness, the dependence on atomic arrangements at the surface is extremely strong, as might be expected based on the modeling results of parts c and d of Figure 2. With modeling, one can consider, for example, the case where the surface of the quartz is amorphous. Consistent with expectation, no single preferred direction appears in this case, similar to growth on thermal SiO\(_2\). More important, calculations show that a layer of amorphous quartz with thickness of only 0.1 nm on Y cut quartz reduces the energy well depth by 60%. This result might explain reports of improved alignment on quartz due to annealing prior to the growth\(^{50}\).
2.3 Alignment on Other Quartz Surfaces

Most previous experimental reports of aligned SWNTs on quartz used the widely available ST cut\textsuperscript{15-23}, which is a type of rotated Y cut that has a cut angle of 42°45′. Growth of SWNTs on such substrates yields aligned tubes with configurations nearly indistinguishable from those on the Y cut. Figure 2.5a shows the energy map of a SWNT of radius 0.6 nm on ST cut quartz, which predicts 0° (x direction) to be the preferred growth direction. This outcome agrees with previously reported experiments\textsuperscript{15-23}. Figure 2.5b shows an SEM image of SWNTs grown on ST cut quartz. No misaligned SWNTs occur within this field of view. In fact, with proper substrate annealing, patterned catalyst, and optimized growth conditions, it is routinely possible to achieve alignment yields, as defined by the percentage of the total length of SWNTs that are aligned, of greater than 99.91%, for regions away from the catalyst particles.

Growth on other cuts of quartz provides additional tests of the theory and also illustrates the degree to which substrate configuration can determine the layouts of the SWNTs. Figure 2.6a shows experimental results for Z cut quartz. Three directions are clearly prominent, as quantified with a histogram (Figure 2.6b) that shows the population of tube segments aligned in different directions. This plot was produced by dividing AFM images of tubes into a series of straight segments, each 150 nm long, and then recording their orientations. Figure 2.6c presents the energy map calculated for this case and the surface atomic structure in the inset. The results indicate minima along three directions: 0° (x direction, [2\bar{1}0]), 60° ([11\bar{2}0]), and -60° ([1\bar{1}20]), consistent with the results of Figure 2.6a.

The case of X cut substrates, shown in Figure 2.6d, provides a different type of result. Although the apparent alignment is poor compared to the Y and Z cuts, the SWNTs still exhibit some rough, overall orientation, in this case along the y direction. A histogram analysis similar to
that in Figure 2.6e summarizes the results. Figure 6f shows the computed energy map and surface atomic structure. This map indicates minima along four directions: 0° (y direction, [01\bar{1}0]), 90° (z direction, [0001]), and 32° and -32°, each with approximately the same energy well depth. We speculate that this situation allows the SWNTs to switch from the global minimum along 0° (y direction) to the (32° directions and that such switching can happen many times during the growth. Such a mechanism is consistent with the experimental results in Figure 2.6d. As with the Y cut quartz, the higher energy required to bend from 0° might explain the relative absence of orientations along the minimum at 90°.

2.4 Conclusions

In summary, we have presented comprehensive theoretical and experimental studies of the process of alignment of SWNTs on quartz with various orientations. The collective body of results is consistent with an underlying physics governed by angle-dependent van der Waals interactions with the substrate. Other effects such as those related to surface polarization and piezoelectricity can contribute, but analysis suggests that their magnitudes are comparatively small. An intuitive picture therefore emerges in which the SWNTs orient along molecular-scale topological grooves that exist in certain directions on the surface of the substrate. The crystalline quality of the surface is paramount, while small features of surface relief or general surface roughness are relatively unimportant. This body of work might provide insights into formation of aligned configurations of SWNT on other crystalline substrates and, more generally, into strategies for nonepitaxial, orientation controlled growth of other classes of nanomaterials.
2.5 Methods.

SWNT Growth

For all experiments SWNTs were grown by CVD at 925 °C for 20 min, with a flow of 20 standard cubic centimeters per minutes (sccms) of Ar and 20 sccms of H2, bubbled through chilled (0 °C) ethanol. The growths were catalyzed by Fe nanoparticles dispersed on the substrate in one of two ways, both designed to minimize the interaction of unreacted catalyst particles with the SWNTs. In the first, a solution of ferritin (Sigma Aldrich) diluted 20000 times in deionized water was dispersed over the surface to form a bead of solution that covers the entire sample. Drops of methanol were then applied one at a time to each region of the substrate to cause particles to precipitate from the solution and coat the surface. Roughly 30 s was allowed between drops. Finally, the total volume of liquid was rinsed away with methanol and the sample was blown dry with N2. Heating to 850 °C for several minutes eliminated the organics, leaving Fe nanoparticles. While nanoparticle densities varied considerably from substrate to substrate, they tended to be ∼10-15 nanoparticles/μm, based on AFM, for the results reported here. In the second approach, thin films of Fe (0.1 nm, nominal) were deposited (electron beam evaporation; Temescal) at a high angle (∼80°) onto 1-2 μm (either lines or dot arrays) openings in photolithographically patterned layers of photoresist (Shipley S1805; ∼500 nm). The photoresist was removed with a brief rinse in acetone. The resulting substrates were annealed at 950 °C for 1.5 h to form sparse coverages of iron nanoparticles in regions corresponding to those defined in the photoresist. In both approaches the samples were heated to the growth temperature in 300 sccms of H2 to reduce the Fe. SEM images were collected using an Hitachi S-4800 SEM at an operating voltage of 1 kV.

AFM Analysis
AFM images were collected using an Asylum MFP3D AFM with Budgetsensor AFM tips. For all images, scan speeds were less than 20 μm/s; for those used to define the histograms, the speeds were less than 10 μm/s; and for those used to determine diameters, speeds were less than 2.5 μm/s. All quartz wafers (Hoffman materials) were cleaned by rinsing with solvents (acetone, isopropyl alcohol, deionized water) and annealed for 8 h at 900 °C. Y-cut wafers were polished using 0.1, 0.25, and 0.5 μm grit diamond paper to remove step edges associated with manufacturer cleaning (5% HF and saturated ammonium bifluoride). Various grits and anneal times (900 °C) yielded samples with different levels of surface roughness.

**Generating Orientational Histograms**

Orientation histograms were generated by tracing SWNTs in SEM and AFM images using the NeuronJ application for ImageJ. This processing provided two-tone images and x,y coordinates for the traced SWNTs. Line segments were created between points with a fixed distance from one another along the length of the SWNTs using MATLAB. There angles were recorded and used to generate histograms. The segments (~250 nm) were selected to be as long as possible, without exceeding the characteristic length of straight regions of the SWNTs. Orientation Histograms were created from AFM images of SWNTs on X (Figure 2.10) and Z (Figure 2.11) cut quartz. Figures 2.10-2.11a show the respective AFM images. The NeuronJ application (ImageJ software) was used to trace SWNTs. Figures 2.10-2.11b show the resulting two tone traced images. The x,y coordinates of the SWNT were used to form segments of a fixed pixel length along the length of the SWNT. MATLAB was used to generate these segments and generate histograms based on their orientation. Figures 2.10-2.11c-f show the resulting histograms for several different segment lengths. The key features are clear for all histograms, however are less prominent if segments are too short or too long. In the case where segment
lengths are too short, random noise associated with the resolution of the image causes features to be obscured. In the case where segment lengths are too long, critical features are missed. For the X and Z cut images, the optimal lengths were ~50 nm and 250 nm respectively. Figures 2.12 and 2.13 show similar analyses for SEM images of Z and X cut quartz, respectively. The same general trends are observed, but they are less apparent due to the poor resolution. AFM images are clearly optimal for this type of analysis.

2.6 References


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2.7 Figures

Figure 2.1 Schematic illustrations of a (5,5) single walled carbon nanotube (SWNT) resting on top of a Y cut quartz substrate. a, Top view, with key dimensions and variables identified. b, End-on cross sectional view, with variables identified. c, Side cross sectional view.
Figure 2.2 Orientation dependence of the van der Waals interaction energy between SWNTs and the surface of Y cut quartz. a, Molecular modeling (symbols) and analytical calculations of interaction energies per unit length of SWNTs as a function of orientation angle (θ) on quartz. We refer to these plots as ‘energy maps.’ The good agreement between the results validates the analytical approach. Minima at 0, 48, -48 and 90 degrees correspond to directions of preferred alignment. b, Energy maps for the case of SWNTs with various radii (R). The depths of the energy minima decrease with increasing R, as shown in the inset plot. c, Change in height of a SWNT relative to the minimum height (h₀) above the quartz (h-h₀) as a function of orientation angle. The results show that the SWNT rests closer to the surface of the quartz in the preferred alignment directions, along 0, 48, -48, and 90 degrees. d, Interaction energy and (h-h₀) as a function of angle for a SWNT (R=0.6 nm) on quartz, where the interactions are treated as hard spheres. The ability of this extremely simple model to capture the preferred alignment directions suggests an intuitive picture of the alignment process in which the SWNTs rest in molecular scale grooves on the surface of the quartz.
Figure 2.3 Scanning electron microscope (SEM) images of SWNTs grown by CVD on Y cut quartz substrates.  

a, Large area SEM view of aligned SWNTs.  Nearly all tubes align along the x direction, independent of chirality or diameter, consistent with theoretical prediction.  The inset provides the diameter distribution of the SWNTs shown here, as measured by AFM.  

b, SEM image of aligned SWNTs on quartz, where short segments along the 45 and -45 directions are visible.  These directions correspond to local minima in the computed energy maps.  The inset is a histogram showing the frequency of straight segments as a function of angle, weighted by segment length.  Segments near the catalyst (within several μm) and winding SWNTs were ignored in this analysis.  Both scale bars, 25 μm.  The orange arrows indicate the flow direction.  

c, Plot of the percentage of the lengths of SWNTs aligned at 0 degrees as a function of SWNT diameter.  These results were generated from 10x10 μm AFM scans of >100 individual SWNTs.
Figure 2.4 SEM and AFM images of SWNTs grown on a Y cut substrate that exhibits clear steps on its surface and the possible effects of those steps on alignment.  a, AFM (main; scale bar, 500 nm) and SEM (upper left inset; scale bar, 20 μm) images of experimental results. The illustration in the upper right inset shows the crossing of a step by a SWNT. In this case, the preferred alignment direction (x direction) is roughly orthogonal to the directions of the step edges. This observation suggests that alignment can occur in directions that do not lie along step edges, and that the growing SWNTs can climb over nanometer scale features of relief, consistent with mechanics modeling. The orange arrow indicates the flow direction.  b, Interaction energy as a function of distance between a step and the axis of the SWNT oriented along the direction of the step. The inset provides a schematic illustration. The minimum in energy near the step is slightly lower than the minima away from the step, but only by a modest amount. These results and corresponding ones based on molecular modeling suggest that step edges can aid in alignment but that they are not necessary for the alignment process.
Figure 2.5 Interaction energy between a SWNT and ST cut quartz, as a function of orientation angle, and experimental results.  

a, Energy map for a SWNT with radius 0.6 nm on quartz.  The results show a single preferred orientation, at 0 degrees.  
b, SEM image of experimental results, showing behavior consistent with theory. Scale bar, 20 μm.  The orange arrow indicates the flow direction.  In a typical case such as this one, more than 99.91% of the total lengths of the SWNTs lie along the preferred direction, not including the regions where the catalyst particles are located.
Figure 2.6 Experimental results for SWNTs grown on Z and X cut quartz, and corresponding calculations of the dependence of interaction energy on orientation angle. 

**a**, SEM image of SWNTs grown on Z cut quartz. The inset shows a SWNT that grew above the quartz and then dropped to the surface after growth. The orange arrows indicate the gas flow direction. 

**b**, Histogram of measured orientations of segments of SWNTs examined by AFM analysis. This procedure reveals three preferred orientation directions, each of which can be seen in (a). 

**c**, Energy map for a SWNT with radius 0.6 nm on Z cut quartz. The predicted orientation angles are consistent with experiment. 

**d**, SEM image of SWNTs grown on X cut quartz. The orange arrow indicates the gas flow direction. 

**e**, Histogram of measured orientations of segments of SWNTs examined by AFM analysis. This procedure reveals a broad distribution of orientations, centered around 0 degrees. Diffuse peaks at +/- 30° indicate a slight preference toward these directions. 

**f**, Energy map for a SWNT with radius 0.6 nm on X cut quartz. The predicted orientation angles span the range of orientations are dominate the experimental results. Scale bars, 20 µm (scale bar in inset, 30 µm).
Figure 2.7 AFM of polished Ycut quartz samples. The RMS roughness is 0.23 nm. Following growth the beginning of step edge formation can be observed, however it does not appear to greatly degrade the overall alignment. a,b show surfaces with barely observable and more well defined step edges respectively. In both cases the alignment is nearly perfect, though it is slightly better in a.
Figure 2.8 SEM images showing the level of alignment as a function of substrate roughness. The roughness was measured via AFM on 6 locations on the substrate prior to growth. Alignment is perfect for samples with roughness up to 0.8 nm and still very good for rougher substrates.
Figure 2.9 Dual Frequency AFM for very rough substrate (0.8 nm RMS).  

**a**, Height image showing roughness. Roughness is enough that SWNTs are not observable.  

**b**, Secondary frequency amplitude signal showing contrast to observe SWNTs. They are perfectly aligned despite rough surface.  

**c**, 3D rendering with topography from height (a) and coloring from secondary amplitude (b).
Figure 2.10 Images demonstrating the creation of orientation histograms. a. AFM image of SWNT on X cut quartz. Scale bar, 500 nm. b. Resulting trace from NeuronJ. c-f. Histograms generated for varying segments lengths 25, 50, 100, and 200 pixels respectively. Each pixel is ~1 nm.
Figure 2.11 Images demonstrating the creation of orientation histograms. 

a, AFM image of SWNT on Z cut quartz. Scale bar, 2 μm. 

b, Resulting trace from NeuronJ. 

c-f, Histograms generated for varying segments lengths 25, 50, 100, and 200 pixels respectively. Each pixel is ~5 nm.
Figure 2.12 Images demonstrating the creation of orientation histograms. **a**, SEM image of SWNT on Z cut quartz. Scale bar, 20 μm. **b**, Resulting trace from NeuronJ. **c-f**, Histograms generated for varying segments lengths 5, 10, 15, and 25 pixels respectively.
Figure 2.13 Images demonstrating the creation of orientation histograms. **a**, SEM image of SWNT on X cut quartz. Scale bar, 20 μm. **b**, Resulting trace from NeuronJ. **c-f**, Histograms generated for varying segments lengths 5, 10, 15, and 25 pixels respectively.
CHAPTER 3

PURIFICATION OF SWNT ARRAYS VIA JOULE INDUCED THERMOCAPILLARY FLOWS

3.1 Introduction

Among the remarkable variety of semiconducting nanomaterials that have been discovered over the past two decades, the collective properties of single walled carbon nanotubes (SWNTs) continue to make them uniquely well suited for diverse applications in high performance electronics, sensors and other device technologies. The most advanced opportunities, however, demand perfectly aligned, horizontal arrays of purely semiconducting SWNTs, in chemically pristine forms. We present here strategies that enable this outcome, where nanoscale thermocapillary flows in thin film organic coatings provide means for highly efficient and selective removal of metallic SWNTs from arrays of SWNT grown by chemical vapor deposition on quartz substrates. The low temperatures and unusual physics associated with this process provide robust, scalable operation, with potential for practical use. Detailed experimental and theoretical studies reveal all of the essential attributes of the underlying thermophysical phenomena. Demonstrations on statistically relevant numbers of transistors quantitatively illustrate the effectiveness of the approach.

Routes to exploit the exceptional electrical properties\textsuperscript{1,2} of SWNTs by implementing them in arrays for advanced applications\textsuperscript{3-9}, involve extremely challenging requirements on
degrees of alignment and purity in semiconducting behavior. Because direct, selective growth of s-SWNTs remains a topic of continuing study, the synthetic strategies that offer the greatest near-term potential fall into two categories: (1) purify the SWNTs and then assemble them into arrays; and (2) assemble the SWNTs into arrays and then purify them. The first has the advantage that it can exploit recently developed physical-chemical techniques (ultracentrifugation\textsuperscript{10,11}, chromatography\textsuperscript{12-14} and others\textsuperscript{15,16}) for purification. The disadvantages are that SWNTs processed in this way are typically short (~1 μm), chemically modified and/or coated, and difficult to assemble into arrays with high degrees of alignment\textsuperscript{15,17-19}. The second overcomes these limitations in assembly through the use of chemical vapor deposition techniques which, when applied on quartz substrates, yield nearly perfectly linear (>99.9% of SWNTs within 0.01° of perfect alignment), aligned arrays of long (100 μm and up to ~mm’s) and chemically pristine SWNTs\textsuperscript{3,20-23}. The main difficulty is in removing the m-SWNTs from arrays of this type. Various techniques attempt to exploit optical\textsuperscript{24}, electrical\textsuperscript{25}, or chemical\textsuperscript{26-28} effects to realize this goal, but they all involve some combination of drawbacks, including incomplete removal of m-SWNTs, degradation of s-SWNTs, inability to operate on aligned arrays and/or reliance on uncertain underlying mechanisms. Among these methods, electrical breakdown is noteworthy because it operates based directly on relevant distinguishing characteristics in charge transport\textsuperscript{25}. Here, Joule heating caused by current passing through the m-SWNTs leads to formation of a narrow gap at some point along the length of each of these tubes. During this process, an appropriate electrostatic bias applied to the s-SWNTs minimizes conduction through them and, therefore, the probability for their breakdown. This scheme, however, has two critical disadvantages, each one of which renders use in any realistic application impractical. First, breakdown requires high powers (~90 μW/μm for channel lengths > 1 μm, increasing as channel
length decreases to values >1 mW/μm\textsuperscript{29-31}. Under these conditions, numerous undesirable behaviors in the associated biasing structures (i.e. electrodes, dielectrics) ensue, ranging from shifts in threshold voltage, to avalanche effects, band-to-band tunneling, failure in gate dielectrics, and significant heat sinking at the contacts. These effects create difficulties in maintaining electrical integrity in the structures and in avoiding transport through the s-SWNTs\textsuperscript{20,29,32,33} and therefore degradation in their properties. More significantly, the breakdown process itself only removes the m-SWNTs in isolated, narrow regions (~100 nm lengths), with positions that are not well controlled\textsuperscript{34}. In other words, the vast majority of the m-SWNTs remain in the arrays; as a consequence, the resulting arrays are unsuitable for any generalized use in subsequently fabricated devices.

### 3.2 Thermocapillary Enhanced Purification

Here, we introduce an approach for eliminating m-SWNTs that offers the key desired attributes, via the use of low temperature thermocapillary effects in thin organic coatings on arrays of SWNTs. We illustrate these concepts through the complete physical removal of all m-SWNTs from linear, horizontally aligned arrays that contain both m-SWNTs and s-SWNTs, without any adverse measurable effects on the latter. Figure 3.1a,b show schematic illustrations and corresponding atomic force microscope (AFM) images of this process, as applied to SWNTs formed by chemical vapor deposition (CVD) on ST-cut quartz substrates with iron nanoparticles as the catalyst and ethanol as the carbon feedstock. The resulting arrays consist of individual, isolated SWNTs, with very few multiwalled nanotubes or bundles of SWNTs, but with a distribution of diameters between ~0.6 and ~2.0 nm and a range of chiralities\textsuperscript{23,31}. The key element in the purification process is an ultrathin (~25 nm) amorphous layer of a small molecule organic species, in this example α,α,α'-Tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene,
which has been used in the past for other, unrelated lithographic purposes\textsuperscript{35}, deposited uniformly over the arrays of SWNTs by thermal evaporation. We refer to this film as a thermocapillary resist (Tc-resist), due to the nature of its operation in the process reported here. Besides its favorable thermophysical properties, as described subsequently in quantitative detail, this material is well suited for present purposes because it combines hydroxyl and phenyl moieties to facilitate formation of uniform, continuous coatings on the surfaces of both the quartz and the SWNTs. This behavior is critical for its role as an effective etch resist at extremely small thicknesses.

Metal and dielectric layers patterned at the edges of an area of interest enable current injection primarily into only the m-SWNTs, through electrostatically induced increases in the heights and widths of the Schottky barriers that form at the metal contacts at one end of the s-SWNTs. These layers represent a removable, transistor structure in which the gate extends only a small distance beyond the source electrode (~5 \( \mu \text{m} \)) compared to the separation between the source and drain (~30 \( \mu \text{m} \)) (See Methods). Applying a positive voltage to the gate (typically ~20 V) a negative voltage to the drain (typically ~40-50 V), while holding the source at electrical ground leads to selective Joule heating only in the m-SWNTs, due to approximately unipolar p-type behavior in the s-SWNTs. This set of bias conditions produces small increases in temperature in the vicinity of the m-SWNTs, and none at the s-SWNTs. The large thermal gradients associated with the nanoscale localization of these heat sources, in turn, drive mass transport in the Tc-resist via the action of thermocapillary forces. In typical experiments (fields of ~1.33-1.66 \( \text{V/\mu m} \) along the SWNTs for 5 min, with substrate heating to 60 °C), the resulting material flows yield trenches centered at the positions of the m-SWNTs and extending throughout the thickness of the Tc-resist with widths at the base that we estimate to be ~100 nm.
Reactive ion etching (RIE; O$_2$/CF$_4$) physically eliminates the m-SWNTs, which are all exposed in this manner, without affecting the s-SWNTs, which remain coated. Removing the Tc-resist and metal/dielectric structures leaves a purified array of SWNTs, consisting only of s-SWNTs, in configurations well suited for planar integration into diverse classes of devices and sensors that demand, or benefit from, exclusively semiconducting operation. In the following, we refer to this overall process as thermocapillary enabled purification (TcEP) of arrays of SWNTs.

A key feature of TcEP is its exceptional efficiency in removing the m-SWNTs completely and exclusively. Such operation is important because most envisioned applications of s-SWNTs in electronics, for example, require purity at the level of 99.99% or better (i.e. fewer than one m-SWNT for every 10,000 s-SWNTs). For present purposes, we define a SWNT as metallic (semiconducting) if the ratio between the on ($I_{on}$) and off ($I_{off}$) currents (i.e. on/off ratio) in a well designed transistor structure that incorporates this SWNT is less than (greater than) ~100. This definition places SWNTs that are sometimes referred to as quasi-metallic into the m-SWNT classification. (In all cases, we observe a clear distinction between the behavior of m-SWNTs and s-SWNTs defined in this way, for populations of SWNTs grown on quartz. In particular, of the hundreds of SWNTs studied here and elsewhere, none exhibits on/off ratios between ~50 and ~1000.)

Detailed electrical characterization (i.e. $I_{on}$ and $I_{off}$ before and after TcEP) and counting statistics (i.e. total numbers of SWNTs before and after) performed on significant numbers of devices (35 devices, each with an active area of ~30×30 μm to enable full visualization by AFM; 377 SWNTs in total) provide quantitative insights into the effectiveness. Figure 3.1c shows a representative transfer characteristic for a device before and after TcEP, measured using the same metal/dielectric structures that enable selective Joule heating. The results illustrate a dramatic reduction in $I_{off}$ (from 0.7 μA to 2×10$^{-5}$ μA), to improve the on/off...
ratio from 2.7 to 3x10^4. All devices showed on/off ratios <10 (median=3.7) before and >2x10^3 (median=6.6x10^4) after TcEP, independent of the number of SWNTs removed (Fig. 3.1d). The relatively small numbers (<30) of SWNTs in each device used to examine the statistics lead to the conclusion that the observed on/off ratios following TcEP correspond to complete removal (i.e. 100%) of m-SWNTs from the as-grown arrays.

Several other results suggest that the process also preserves most or all of the s-SWNTs. First, of the 377 SWNTs present initially, 63% (i.e. 238 SWNTs) remain after TcEP. This outcome is consistent with the expected percentage (~66%) of s-SWNTs in collections of SWNTs grown by CVD\textsuperscript{3,37}. Second, among 28 devices where the SWNT type can be determined from electrical behaviors measured before and after TcEP (i.e. those devices that incorporate ≤2 SWNTs), all of the m-SWNTs and none of the s-SWNTs show trenches (for optimized conditions; see Chapter 4, Fig. 4.1). Third, reductions in $I_{on}$ induced by TcEP are modest; for the example of Fig. 3.1c the ratio of $I_{on}$ after the process to its value before is $I_{on,a}/I_{on,b}$ ~25%. The weighted average from all of the devices is $I_{on,a}/I_{on,b}$ ~30%. These results can be interpreted by examining the dependence of $I_{on,a}/I_{on,b}$ on the percentage of SWNTs removed by TcEP (Fig. 3.1e). The trends are consistent with models that assume 100% preservation of s-SWNTs, expected populations of s-SWNTs and m-SWNTs, and ratios of conductances of m-SWNTs to s-SWNTs (in their on state) that are within an experimentally observed range of 6:1 and 2:1 (See Chapter 4, Fig. 4.3). Collectively, then, all observations are consistent with highly selective and efficient operation in TcEP, in which all m-SWNTs are eliminated, and most or all s-SWNTs are preserved.

### 3.3 Fundamental Aspects of Joule Induced Thermocapillary Flow
The thermocapillary effects and the ability to exploit this physics at the nanoscale using remarkably small increases in temperature (a few °C) are critical to practical and effective operation of TcEP. Detailed experimental and theoretical studies reveal the quantitative aspects. We start by examining the distributions of temperature generated during TcEP and their role in the behavior of the Tc-resist. Figure 3.2a shows a scanning Joule expansion microscope (SJEM\(^3\)) image that reveals patterns of thermal expansion that result from Joule heating in an array of SWNT, at a drain-source bias condition \(V(t)=V_{DS} \cos(2\pi ft)\) with \(V_{DS}=5\) V and \(f=386\) kHz, where associated Joule heating with power density \(0.1 \cos(4\pi ft)\) yields AC thermal expansion at frequency \(2f\), according to \(E(t)=E_1+E_0 \cos(4\pi ft)/2\) Here the components including \(E_1\) and \(E_0\) are the DC and AC thermal expansions, respectively. Figure 3.2b shows AFM topographical images of the same array coated with Tc-resist, after application of several different, increasing values of \(V_{DS}\) (direct current for 5 min; substrate temperature 60 °C). (The image signal corresponds to the peak-peak value of the AC expansion, \(E_0\)). A key observation is that the distributions in expansion, and therefore temperature, (Fig. 3.2a) correspond directly to the geometries of trenches that appear in the Tc-resist (Fig. 3.2b). For instance, trenches observed by AFM progressively form with increasing \(V_{DS}\) in an order consistent with the relative temperatures of the SWNTs revealed by SJEM, e.g. trenches at the second and fifth SWNT from the right appear first and last, respectively. Related effects can be observed along an individual SWNT, where trenches nucleate in areas of enhanced temperature increase (‘hot spots’; arrows in Fig. 3.2a and the top frame of Fig. 3.2b). These indications establish a clear, although qualitative, connection between temperature and operation of the Tc-resist.
The first step to quantitative understanding of TcEP is an experimentally validated model for nanoscale heat flow in this system. Raw data from SJEM measurements indicate relative temperature rises associated with AC Joule heating ($V_{DS}=3V$, $f=30kHz$), but not their absolute values. Figure 3.2c shows a representative cross sectional profile of $E_0$ for the case of a SWNT with length $\sim 3.5\ \mu m$, where the power per unit length (power density) is

$$Q(t) = Q_0 \left[1 + \cos\left(4\pi ft\right)\right]/2 \text{ with } Q_0 \text{ estimated to be } \sim 13\ \mu W/\mu m \text{ based on the total input power into the device, which includes three SWNTs that yield SJEM signals on an SiO}_2/\text{Si substrate, and the corresponding SJEM image (See Chapter 4, Fig. 4.5). Analytical models of temperature distributions associated with Joule heating in a SWNT, treated as a line heat source with length } L \text{ and an input power density of, } Q(t) = Q_0 \left[1 + \cos\left(4\pi ft\right)\right]/2 \text{ can be developed. (See Chapter 4, Fig. 4.6) Boundary conditions involve continuous temperature and heat flow at all material interfaces except those with the SWNT, negligible heat flow at the top surface and a constant temperature at the base of the substrate. For the SWNT interface, discontinuous heat flow, } Q(t), \text{ is assumed, as a means to introduce the Joule heat source. The results, together with materials constants taken from the literature (See Chapter 4, Table 4.1) and analytical treatments of the resulting thermal expansion, yield expansion profiles that have both peak magnitudes } (E_0 \sim 50\ \text{pm}) \text{ and spatial distributions (characteristic widths } \sim 340\ \text{nm}) \text{ that are remarkably consistent with the SJEM results (} \sim 40\ \text{pm and } \sim 320\ \text{nm, respectively), when } Q_0 \sim 13\ \mu W/\mu m, \text{ the estimated experimental value. Figure 3.2d shows the associated AC temperature rises } (\theta_0) \text{ and thermal gradients } (d\theta_0/dx), \text{ such that, } \theta(t) = \left[\theta_1 + \theta_0 \cos\left(4\pi ft\right)\right]/2 \text{ (} \theta_1 \text{ is the DC temperature rise. See Chapter 4 for additional details). When applied to the case of DC heating } (f=0), \text{ and}
quartz substrates, the same analytical model yields an expression for the rise in temperature of the surface of the Tc-resist, \( \theta = T - T_\infty \) where \( T_\infty \) defines the temperature of the background,

\[
\theta(x, y) = \frac{1}{2k_s \pi} \int_{-L/2}^{L/2} d\eta \int_0^\infty d\xi J_0(\xi \sqrt{(\eta - y)^2 + x^2}) \frac{k_f}{k_s} \frac{\sinh(\xi h_f)}{\cosh(\xi h_f)}
\]

Here, \( k_s \) and \( k_f \) are the thermal conductivity of Tc-resist and quartz substrate, respectively, and \( h_f \) is the thickness of Tc-resist. This solution, which is also consistent with 3D finite element analysis (ABAQUS), suggests that experimentally observed power densities needed to achieve trenches in the Tc-resist when on quartz (~3-10 \( \mu W/\mu m \) per SWNT), yield remarkably small increases in temperature at the SWNTs (~2-5 \(^\circ\)C). Independent measurements of thermocapillary flows induced by heated AFM tips, where the peak temperatures are measured directly, exhibit similar behaviors (See Chapter 4, Fig. 4.10).

Even these small increases in temperature (~4 \(^\circ\)C) create large thermal gradients (~20 \(^\circ\)C/\( \mu m \)), due to the nanoscale dimensions of the sources of heat, defined by the diameters of the SWNTs, ~0.6-2 nm. These gradients are, in fact, sufficient to induce thermocapillary forces capable of driving complete flow of the Tc-resist away from the heated regions (i.e. the m-SWNTs). The detailed physics is critically important for many reasons, one of which is immediately evident from inspection of Figs. 3.2a,b. At large \( V_{DS} (>1 \text{ V}/\mu \text{m}) \), the trenches associated with SWNTs that show pronounced hot spots exhibit uniform widths, with no apparent consequence of spatial non-uniformities in heating. Likewise, SWNTs that show vastly different temperatures at a given \( V_{DS} \) display similar trench widths at sufficiently large \( V_{DS} (>1 \text{ V}/\mu \text{m}) \). Figure 3.2e shows results for the second SWNT from the right, extracted from Fig. 3.2a.
and the bottom frame of Fig. 3.2b. Clearly, the variations (between the mean value and maximum value) in the expansion measured along the length of the SWNT by SJEM are much larger, in fractional sense 10x larger, than those in the trench widths, quantified by separations between the raised regions of the Tc-resist at the edges of the trench ($W_{Tc}$). This type of physics provides an ability to realize trenches with small, uniform widths even across large-scale arrays that incorporate m-SWNTs with wide ranges of conductances and diameters, and consequently, peak temperatures and thermal gradients. Figure 3.2f shows the average $W_{Tc}$ for a number of different, individual SWNTs as a function of $Q_0$. Similar values occur over a wide range of powers (~10-40 μW/μm), even beyond those associated with optimized conditions for TcEP. This behavior is much different than that expected from other thermally driven processes, such as sublimation or ablation, which typically involve abrupt temperature thresholds (See Chapter 4, Fig. 4.13); it is among several quantitative aspects of nanoscale thermocapillary flow that are essential to understanding and optimizing the process.

The governing equation of motion for thermocapillarity in systems where the dimension along the SWNTs can be considered infinite corresponds to unidirectional flow in which the thickness profile in the Tc-resist can be written $h(x,t)$ and.

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left[ \tau \frac{h^3}{2\mu} + \frac{h}{3\mu} \frac{\partial}{\partial x} \left( \frac{\partial^2 h}{\partial x^2} \right) \right] = 0$$  \hspace{1cm} (2)

where $\bar{h} = h/h_f$, $\bar{x} = x/h_f$, $\tau = \gamma Q_0/(\mu k/h_f)$, $\bar{\mu} = \mu/\mu_0$, $\bar{\gamma} = k_1 \gamma/(Q_0 \gamma_1)$, $\bar{\theta} = k_1 \theta/Q_0$, $\tau = \partial \bar{\theta}/\partial \bar{x}$ is the thermocapillary stress, $\mu$ is viscosity at temperature $T$, $\mu_0$ is the viscosity at the background temperature $T = T_\infty$, and $\gamma$ is the surface tension, which often exhibits a linear dependence on temperature (i.e., $\gamma = \gamma_0 - \gamma_1 \theta$). Figure 3.3a shows the geometry. The
appropriate initial condition is \( h(x, T = 0) = 1 \). The boundary conditions are, \( h(x = \pm \infty, T) = 1 \), and zero pressure, \( \frac{\partial^2 h}{\partial x^2}(x = \pm \infty, T) = 0 \). With Eq. (1) for the temperature, numerical solutions to this system yield \( h = h/h_f \), based on assumptions that (a) at each point along \( x \), the temperature throughout the thickness of the Tc-resist is equal to the temperature at its interface with the substrate and (b) flow in the Tc-resist does not change the temperature distributions. Figure 3.3b shows results for the case of polystyrene\(^{39} \), which exhibits behaviors like the Tc-resist but with less ideal properties (See Chapter 4, Fig. 4.12), and, unlike the Tc-resist, has a known temperature dependent surface tension, according to \( \gamma = 50.40 - 0.0738\theta \) mJ/m\(^2\). For this example, \( \bar{\mu} = 1 \), consistent with the small rise in temperature, and \( Q_0 = 16.7 \mu W/\mu m \) (from experiment). The trenches gradually widen and deepen with time, as the displaced material forms ridges at the edges. AFM measurements of a representative SWNT coated with Tc-resist, after Joule heating for various time intervals \( (V_{DS} \sim 0.7 \) V/\( \mu m \), \( 30^\circ C \) background heating) show similar behaviors and profiles (Fig. 3.3c,d). At longer times, wider trenches result, to the point where SWNTs can be clearly observed at the base in AFM measurements (Fig. 3.3e). Although the specific time durations needed to form complete trenches \( (\bar{t} \sim 1) \) yield computed values of \( W_{Tc} \) that are larger than those observed experimentally, the essential time dependence is captured accurately by the theory. For example, Fig. 3.3f shows the measured time dependence of \( W_{Tc} \) for two SWNTs, where both show behavior expected theoretically, namely \( W_{Tc} \sim t^{0.25} \) (See Chapter 4, Fig. 4.8-4.9). Another prediction of the theory is that, for a given time \( t = 300 \) s, the value of \( W_{Tc} \) depends only weakly on \( Q_0 \), over a remarkably large range, i.e. from \( \sim 10 \mu W/\mu m \) to \( \sim 35 \mu W/\mu m \) (See Chapter 4, Fig. 4.9). This finding is consistent with observations discussed in the context of Fig. 3.2. Finally, besides capturing the underlying physics, these models also establish a set of
guidelines for the selection of optimal materials for Tc-resists, i.e. large temperature coefficients of surface tension and low viscosities yield narrow trenches within reasonable experimental times. Furthermore, decreasing the thickness reduces the trench widths. Empirical studies of various materials for Tc-resists (See Chapter 4, Fig. 3.12) led to the selection of the molecular glass reported here.

3.4 Large Area TcEP

The envisioned practical use of TcEP is in a preparatory mode, where it serves as one of the several steps, such as substrate cleaning, SWNT growth, transfer and others, that occur before device processing. Such a scheme decouples TcEP from any detailed consideration in component or circuit layout, and is made possible by the ability to eliminate all m-SWNTs, in their entirety, and to do so with removable electrode / dielectric structures. Two approaches can be considered. In the first, one or a small number of sets of electrodes, each with large lateral extent as illustrated in Fig. 3.4a,b, enable elimination of m-SWNTs over significant areas. Here processing occurs on hundreds or thousands of SWNTs at once, using pulsed currents to avoid cumulative heating (See Chapter 4, Fig. 4.11). Figure 4c shows the electrical characteristics of the structure in Fig. 3.4a before and after TcEP, where $I_{on,a} / I_{on,b}$ is ~20% and the on/off ratio after the process is ~1x10³, similar to the results achieved on the small-scale arrays discussed previously. Figure 3.4d illustrates an alternative approach, in which smaller pairs of interconnected electrodes provide for TcEP in distributed regions, lithographically aligned at a coarse level to areas of interest in a final application. Outcomes in this case, in terms of effects on $I_{on}$ and $I_{off}$, are in the range of those achieved in other geometries (see Chapter 4, Fig. 4.15, Table 4.2).
3.5 Conclusions

In summary, the TcEP method introduced here provides scalable and efficient means for converting heterogeneous arrays of SWNTs into those with purely semiconducting character. Careful control of the process might also allow refined forms of purification, based not just on differences between m-SWNTs and s-SWNTs, but on differences in threshold voltages or other more subtle characteristics among the s-SWNTs themselves. Other promising opportunities for future work include development of optimized conditions and materials for performing TcEP directly on high density arrays (e.g. >10 SWNT/μm), and of schemes that eliminate the need for electrode structures, using electromagnetic exposures or other processes that can take advantage of the unique and low temperature operation of nanoscale thermocapillary flows.

3.6 Methods

Forming horizontally aligned arrays of SWNTs. Photolithography (AZ 5214 positive photoresist), electron beam evaporation (0.6 nm Fe; AJA), and subsequent liftoff defined regions of catalyst in the geometry of strips oriented perpendicular to the preferred growth direction on ST-cut quartz substrates (Hoffman). Annealing at 950 °C for 1 hr (quartz tube furnace with ~1 inch outer diameter), cooling the furnace, purging it with hydrogen, and then heating to 925 °C prepared the iron catalyst for chemical vapor deposition. Introduction of growth gases (20 sccm H₂, 20 sccm Ar, bubbled through ethanol) at 925 °C for 20 min yielded well aligned arrays of SWNTs.

Fabricating source, drain, gate and gate dielectric structures. Photolithography, electron beam evaporation (2 nm Ti, 48 nm Pd; AJA) and liftoff defined source and drain electrodes (channel length, L, of 30 μm, and with various channel widths, W). Photolithography (AZ 5214)
and reactive ion etching (100 mtorr, 20 sccm O₂, 100 W, 30 s; Plasma-Therm RIE) removed SWNTs everywhere except for regions between these electrodes. Prebaking (250 °C, 2 hr, in a glove box) a spin cast (4000 rpm, 60 s) solution to a spin-on glass (SOG; Filmtronics; methylsiloxanes 215F, 15:1 diluted in IPA)⁴⁰ and then curing the material formed films of SOG (35 nm) uniformly across the substrate. Atomic layer deposition (80 °C; Cambridge NanoTech) created films of Al₂O₃ (30 nm) on top of the SOG. Photolithography (AZ 5214) and etching (6:1 BOE for 50 s, followed by rinsing for 5 min in deionized water) removed most of the SOG/Al₂O₃ bilayer between the source/drain electrodes, to expose substantial lengths of the SWNTs in the region between the source and drain (i.e. ~15-20 μm). Prebaking (110 °C, 10 min) a spin cast 5wt% solution of polyvinyl alcohol (PVA; Mₙ between 89,000 and 98,000, 99%, hydrolyzed, Sigma-aldrich; solvent: D.I. water) mixed with photosensitizer (ammonium dichromate), >99.5%, Sigma-aldrich, PVA: photosensitizer=40:1 (weight ratio)⁴¹ (800 rpm, 60 s spread cycle, 4000 rpm, 60 s spin cycle) followed by photolithographic patterning and postbaking (110 °C, 30 min) defined a layer of PVA (~400 nm) on top of and aligned with the SOG/Al₂O₃ bilayer. Photolithography (AZ 5214), electron beam evaporation (50 nm Ti or Cr), and lift-off defined a gate electrode on top of this dielectric stack.

**Fabricating devices that incorporate a single SWNT.** The fabrication procedures followed those described above. The use of arrays of SWNT grown at low density (0.1-0.2 SWNT/μm), and subsequently etched in patterns that removed all of the SWNTs except those in narrow strips (~3 μm widths) yielded devices with small numbers of SWNTs. Electrical and AFM analyses identified a subset of such devices that incorporated only a single SWNT bridging the source and drain electrodes.
Thermocapillary flow and etching to remove m-SWNTs. Thermal evaporation (0.5 Å/s, Kurt Lesker) formed thin layers (25 nm) of $\alpha,\alpha,\alpha'$-Tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene (TCI international) as the Tc-resist. Applying a voltage between the source/drain electrodes ($V_{DS} = -40$ to $-50$ V, corresponding to fields of $-1.33$ to $-1.66$ V/μm) while biasing the source/gate to $+20$ V under vacuum ($\sim1 \times 10^{-4}$ torr, Lakeshore) and holding the substrate temperature at 60 °C, all for $\sim5$ min, yielded trenches in the Tc-resist at the locations of the m-SWNTs. Reactive ion etching (10 mtorr, 1 sccm O$_2$, 1 sccm CF$_4$, 75 W, 20 s; Plasma-Therm RIE) eliminated the m-SWNTs exposed in this manner, without affecting the s-SWNTs. Immersion in acetone for 30 min removed the Tc-resist, to complete the process.

Scanning Joule Expansion Microscopy.

Devices were wire bonded to a sample holder (Spectrum Semiconductor Materials) to allow contact mode AFM scanning (Asylum MFP 3D and Cantilever Asylum # Olympus AC240TS) while applying suitable biases to the electrode structures. Evaluation of the force/displacement curve for the cantilever prior to scanning defined the relationship between deflection and detector signal. A function generator (Agilent 33250A) provided the AC bias and the reference signal for the lock-in amplifier (Stanford SR844). The lock-in amplifier collected the amplitude and phase of the signal associated with the thermal expansion of the substrate which occurred at twice the frequency of the applied electrical bias. For SJEM of SWNTs on quartz substrate, thermal evaporation formed thick layers ($\sim100$ nm) of Tc-resist on devices consisting of arrays of SWNTs between two electrodes (i.e. two terminal devices, with $L=30$ μm, $W=30$ μm). The bias consisted of a sinusoidal voltage with amplitude of 5 V and frequency of 386 kHz. For SJEM of SWNTs on SiO$_2$ (200 nm)/Si, the sample consisted of a two terminal device with a
spin cast overcoat of poly(methylmethacrylate) (PMMA; Microchem. 950 A2) with thickness of ~120 nm. The bias consisted of a sinusoidal voltage with amplitude of 3V and frequency of 30 kHz. The doped silicon substrate was electrically grounded.

**Studying the kinetics of trench formation.** Thermal evaporation deposited thin layers of Tc-resist (~25 nm) on two terminal devices ($L=30 \ \mu m$, $W=100 \ \mu m$) configured for electrical connection while in the AFM (Asylum research ORCA sample mount). Images collected by fast scanning (~30 s acquisition times) defined the topography of a small region of interest. In between scans, application of electrical biases for durations short compared to the normalized flow rates (0.1 s at short times and increasing to 30 min at long times) caused the trenches to increase in width by controlled amounts. A total of ~400 scans, corresponding to the device under bias for a total, accumulated time of ~8 hr, revealed the kinetics of trench formation, throughout and well beyond the time of interest for TcEP. The data enabled quantitative validation of models of thermocapillary flow. Detailed analysis allowed for accurate extraction of the average trench widths, and complete surface profiles, as a function of time.

**Removing the gate electrode and dielectric.** Following TcEP, the purified SWNTs (i.e. consisting only of s-SWNTs) were protected by a patterned layer of photoresist (AZ 5214) prior to removal of the gate metal (for Ti, Transene, Inc; titanium etchant TFTN; for Cr, Transene, Inc; chrome mask ethant-CE-5M 9). Wet etching ($H_2SO_4:H_2O_2=2:1$, 60 °C, 5 ~10 s) removed the crosslinked PVA. Etching in buffered hydrofluoric acid (BOE 6:1, 30 s) removed the SOG/Al$_2$O$_3$ bilayer. Stripping the photoresist completed the process.

**Finite element modeling of thermal effects.** The 3D finite element model for the temperature distributions used eight-node, hexahedral brick elements in a finite element software package.
(ABAQUS) to discretize the geometry. The SWNT was treated as a volume heat source, with a zero heat flux boundary at the top surface of Tc-resist, and a constant temperature $T_w$ at the bottom of the quartz substrate.

**Numerical modeling of thermocapillary flows.** The equations of motion represent a pair of coupled partial differential equations

$$\frac{\partial \vec{h}_1}{\partial \tau} = \frac{\partial}{\partial \vec{x}} \left( -\frac{\vec{r} \vec{h}_1^2}{2 \mu} - \frac{\vec{h}_1^3}{3 \mu} \frac{\partial \vec{r}}{\partial \vec{x}} \vec{h}_2 - \frac{\vec{h}_1^3 \frac{\partial \vec{r}}{\partial \vec{x}}}{3 \mu} \vec{h}_2 \right)$$

and

$$\frac{\partial^2 \vec{h}_1}{\partial \vec{x}^2} - \vec{h}_2 = 0$$

where $\vec{h}_1 = \vec{h}$. The boundary conditions are $\vec{h}_1 (\vec{x}, \vec{r} = 0) = 1$, $\vec{h}_2 (\vec{x}, \vec{r} = 0) = 0$, $\vec{h}_1 (\vec{x} = \pm \infty, \vec{r}) = 1$ and $\vec{h}_2 (\vec{x} = \pm \infty, \vec{r}) = 0$. A Fortran routine (PDE_1D_MG) was used to solve these two partial differential equations directly.

### 3.7 References


3.8 Figures

Figure 3.1 Process for exploiting thermocapillary effects in the purification of arrays of SWNTs. (a,b) Schematic illustration and corresponding AFM images of various stages of the process, which we refer to as thermocapillary enabled purification (TcEP), as applied to an array of SWNTs that consists of five m-SWNTs and three s-SWNTs. Uniform thermal evaporation forms a thin, amorphous organic layer that functions as a thermocapillary resist (Tc-resist). A series of processing steps defines a collection of electrodes and dielectric layers for selective injection of current into the m-SWNTs.
**Figure 3.1 continued.** The Joule heating that results from this process induces thermal gradients that drive material flow in the Tc-resist away from the m-SWNT, to form open trenches with widths, measured near the substrate, of ~100 nm. Reactive ion etching physically eliminates the m-SWNT exposed in this fashion, while leaving the coated s-SWNTs unaltered. Removing the Tc-resist and electrode structures completes the process, to yield arrays comprised only of s-SWNTs. (c) Typical transfer characteristics for a transistor built with an array of SWNTs in a partial gate geometry, evaluated before and after TcEP. The quantities $I_{on,b}$ and $I_{on,a}$ correspond to currents measured in the on states before and after TcEP, respectively. Here, the on/off ratio improves by $2 \times 10^4$ times, while $I_{on,a} / I_{on,b}$ remains relatively large, i.e. ~0.25. (d) Ratios between currents in the on and off states before and after TcEP ($I_{on,b}$ and $I_{off,a}$, respectively) as a function of the ratio of the difference between number of SWNTs before and after TcEP ($N_b$ and $N_a$, respectively) to the $N_b$. All devices show on/off ratios $> 2 \times 10^3$, with most $> 1 \times 10^4$. This result is consistent with complete removal of all m-SWNT. (e) Ratio of $I_{on,a}$ to $I_{on,b}$ as a function of $(N_b-N_a) / N_b$, for the entire set of devices with $N_b > 7$. The results are consistent with modeling (lines) that assumes 100% retention of s-SWNTs through the TcEP process, expected relative populations of s-SWNTs and m-SWNTs in the arrays, and ratios of conductivities of m-SWNTs and s-SWNTs (in the their on state) that lie between experimentally expected values.
Figure 3.2 Thermal origins and power scaling in operation of Tc-resists. (a) SJEM image of an array of SWNTs in an operating, two terminal device on quartz. The electrodes (separation ~30 μm) are above and below the image, out of the field of view. The coordinates x and y lie perpendicular and parallel, respectively, to the direction of alignment of the SWNTs. (b) AFM topographical images of the same device shown in the SJEM image of (a), coated with a thin (~25 nm) layer of Tc-resist, collected after operation at bias conditions of 0.27 (top), 0.5 (middle) and 1.0 V / μm (bottom). Comparison of these images to those collected by SJEM reveals a clear correlation between AC expansion (ΔE; and, therefore, temperature) and formation of trenches in the Tc-resist (DC heating). (c) AC Thermal expansion, ΔE, induced by Joule heating in an individual SWNT with input power density \( Q_0 \sim 13 \, \mu W / \mu m \) (peak to peak) measured by SJEM (line) as a function of position \( x \), where \( x=0 \) is the location of the SWNT, on a SiO₂/Si substrate and results of thermomechanical modeling (symbols), illustrating excellent agreement in both magnitude and shape. (d). Computed AC temperature rise, \( \theta_0 \), and thermal gradients (d\( \theta_0 / dx \)) at the surface of the Tc-resist using experimentally validated models, for the case of the SWNT in (c). The results indicate small increases in temperature for levels of Joule heating that induce trenches in the Tc-resist (~3-10 \( \mu W / \mu m \)). (e) The top graph shows AC thermal expansion (arbitrary units) measured by SJEM along the length (y) of the fourth SWNT from the left in the array that appears in (a) and (b). The bottom graph shows the width of the corresponding trench that appears in the Tc-resist (\( W_{TC} \) measured at the top of the film) for an applied bias of ~1 V / μm. The results show variations in \( W_{TC} \) that are nearly ten times smaller than those in expansion (and therefore temperature). (f) Measurements of the average \( W_{TC} \) as a function of \( Q_0 \). The results show no systematic dependence on \( Q_0 \) over this range. The highlighted region corresponds to the values of \( Q_0 \) associated with optimized conditions for TcEP.
Figure 3.3 Nanoscale thermocapillary flows in Tc-resists induced by Joule heating in SWNTs. (a) Schematic illustration of the geometry of the system, with key parameters defined. The SWNT, the Tc-resist and the substrate are grey, green and blue, respectively. (b) Theoretically calculated normalized surface profiles of the Tc-resist ($\tilde{h}$), as a function of normalized distance ($\tilde{x}$) and time ($\tilde{t}$), showing the evolution of the trench geometry with thermocapillary flow. (c) AFM images of a SWNT coated with Tc-resist (~25 nm), at times for Joule heating (0.66 V/μm) of 1, 10, 30, 60, 120 and 300 s, induced by current injection at electrodes that lie outside of the field of view. Thermocapillary flow creates a trench that aligns to the SWNT and grows in width over time. (d) Averaged cross sectional profiles extracted from measurements like those shown in (c). The results compare favorably to the modeling in (b). (e) AFM image, rendered in a 3D perspective view collected at a duration of 1800 s. The width in this case is sufficiently large that AFM measurements reveal clearly that thermocapillary flow completely and cleanly exposes the SWNT at the base of the Tc-resist. (g) Widths of trenches measured by AFM from the ridges that form at the top surface ($W_{Tc}$) as a function of time of Joule heating in two different SWNT, at a field of 0.66V/μm. Both model and experiment show a power law time dependence with an exponent of 0.25.
Figure 3.4  Two approaches to scaled implementation of TcEP.  (a) Optical microscope image of a set of electrodes for TcEP on a large-scale array of SWNTs, which in this example allows purification of ~500 SWNTs.  (b) Scanning electron microscope image of a small region of the structure shown in (a).  (c) Transfer characteristics before and after removal of m-SWNTs by TcEP from the region between the electrodes shown in (a).  The results indicate outcomes consistent with observations of small-scale implementations of TcEP, i.e. high on/off ratios ~$1\times10^3$ and modest reductions in on current ($I_{on,a}/I_{on,b} \sim 20\%$).  (d) Optical micrograph and schematic illustration of alternative mode for scaled implementation of TcEP.  Here, an interconnected array of 25 sets of electrodes allows TcEP over a collection of small regions, in a parallel fashion.  Associated transfer curves are similar to those shown in (c).
CHAPTER 4
DETAILS OF THERMOCAPILLARY ENHANCED PURIFICATION

4.1 Introduction

The basic effectiveness and critical aspects associated with TcEP were described in detail in Chapter 3, however, more detailed understanding of the process requires additional study. In this chapter, we describe a variety of additional experiments to elucidate greater understanding of the process. In particular, a variety of experiments with individual SWNT reveal critical parameters associated with TcEP and aspects of device operation associated with electrode structures used for TcEP. Beyond this, rigorous models of thermal distributions and resulting flow can be compared with rigorous study of the evolution of trenches to gain insight about the process. Finally, analysis of experimental results couple with insights provided by analytical models provide key insight into the critical properties required for effective Tc-resists.

4.2 Individual SWNT Thermocapillary Trench Experiments

Thermocapillary flows in Tc-resists were studied (5 min, 60 °C background heating) using devices that incorporate single or several SWNTs. Devices were fabricated in geometries to ensure that only 1 or 2 SWNTs were present in the channel, as confirmed by AFM. In the case of single SWNT devices, the electronic type could be determined directly from the electrical properties (on/off ratio > 100, s-SWNT; on/off ratio < 10, m-SWNT). For devices with 2 SWNTs that exhibited high on/off ratio, both SWNTs must be s-SWNTs. For similar devices
with low on/off ratio before TcEP and high on/off ratio after TcEP, one SWNT must be a m-SWNT and the other a s-SWNT. Devices with two m-SWNTs were not used for these experiments. Biases were applied to increase the resistance of the s-SWNTs (i.e. their “off” state, at +20 Vgs), resulting in relatively low (high) current levels for all s-SWNTs (m-SWNTs). As a result, all 2 SWNT devices fell into one of two cases: their currents were dominated by a single m-SWNT or they contained two s-SWNTs. For the second case, one s-SWNT is likely to dominate, but at worst, the s-SWNT have roughly equal current levels in which case the data served as an upper limit for the actual current and could be as little as half that level. The large number of devices that were studied and the observation that most s-SWNTs showed current levels more than ten times below the threshold for trench formation suggest that assumptions concerning relative current distributions in s-SWNTs are unlikely to affect the broad conclusions. The thresholds were accurately defined by devices with just one SWNT. We performed systematic studies of trenches formed under a range of input powers for single s-SWNTs and single m-SWNTs. A range of outcomes for input powers between 0.1-30 µW/µm (SWNT length = 30 µm) were observed by AFM (Fig. 4.1a). For all experiments, powers below 3.3 µW/µm led to no trenches. For powers between 3.3-10 µW/µm most devices exhibited trenches, but only partly along the lengths of the SWNTs. For all experiments with powers greater than 10 µW/µm, trenches with widths Wt~250-300 nm, were observed along the entire lengths of the SWNTs. This analysis provides information on threshold powers for trench formation, which, via analytical modeling, can be correlated to peak temperatures of ~2-5 °C. By sorting these same results by input field and SWNT electronic type (Fig. 4.1b), optimized conditions can be established. At fields below the optimal range, the heating is insufficient to yield trenches along the entire lengths of all of the m-SWNTs; at higher fields, the most
conductive s-SWNTs begin to show partial trench formation. However, for optimized conditions, all s-SWNTs yielded no trenches, while all m-SWNTs yield complete trenches, as required for proper operation of TcEP.

4.3 Deposition Conditions for the Tc-resist and its Properties

Fig 4.2a shows the chemical structure of the Tc-resist. The material was deposited via thermal evaporation. Figure 4.2b shows AFM images of a film deposited on a SiO₂/Si substrate. The surface roughness is comparable to that of the underlying substrate, i.e. 2-3 Å. Experiments that involved heated substrates (quartz or SiO₂/Si) with thin coatings of Tc-resist (~25 nm thickness) showed an onset of dewetting between 80-120 °C, depending on substrate hydrophobicity. Clean, hydrophilic surfaces yielded higher dewetting temperatures. In vacuum (~1x10⁻⁴ torr), sublimation began at ~100 °C, as determined by experiments using lithographically patterned, calibrated resistive heaters of Pt (lengths ~1-3 mm, widths ~6-10 µm). Differential Scanning Calorimetry (dry nitrogen) yielded a specific heat of ~1.5 J/C/cm³ (Fig. 4.2c, Tₘ= 225 °C, Tₙ= 95 °C, Tₑ=155 °C). Time resolved, picosecond pump-probe experiments based on thermoreflectance¹ using relatively thick films (300 nm, Fig 4.2d) yielded thermal conductivities of ~0.2 W/m/K, similar to most organic thin films.

4.4 Single SWNT Conductance Statistics

The large number of SWNTs studied by TcEP on devices with small arrays of SWNTs provided statistics on the process. For each array, the number of SWNTs and the values of Iₜₜₙ, b and Iₜₜₙ, a (shown for a typical device, Fig 4.3b) together with an assumption that all of the removed SWNTs are m-SWNTs and all of the remaining SWNTs are s-SWNTs, yields estimates for the average conductance of these two types of SWNTs, for each device. Figure 4.3a shows a histogram of the conductances of individual SWNTs determined in this way. (We note that a
device with 3 s-SWNTs and an average conductance of 50 kΩ/μm is counted 3 times.) The mean conductances for m-SWNTs and s-SWNTs (in their on state) are 17 kΩ/μm and 75 kΩ/μm, respectively. These distributions are in the range of those reported for single SWNTs studied previously\(^2\); with values of 35 kΩ/μm (m-SWNTs) and 55 kΩ/μm (s-SWNTs) for backgated devices (Fig. 4.3c)\(^2\); and 140 kΩ/μm (m-SWNTs) and 1000 kΩ/μm (s-SWNTs) for top gated devices\(^2\). Using the experimentally observed ratios of numbers of m-SWNTs to s-SWNTs, and a ratio of mean conductances of ~4:1, the assumption that TcEP preserves all s-SWNT is consistent with observations.

### 4.5 Partial Gate Device Properties

The electrode geometries used for TcEP involved a partial gate structure shown schematically in Fig. 3.1a. This configuration results in reduced gate-drain fields, which minimize Schottky barrier tunneling, band-to-band tunneling and avalanche phenomena\(^3\). The operation avoids ambipolar conduction at the bias conditions needed for TcEP (Characterization at conditions consistent with TcEP, 60 °C background heating, ~1x10\(^4\) torr). These effects are clearly observed in transfer characteristics for devices based on an individual s-SWNT in partial gate (Fig. 4.4a) and full gate (Fig. 4.4b) layouts. Here, the same SWNT, same pair of source-drain electrodes, and dielectric were used for both devices. The only difference is the length of gate extension into the channel. Both configurations exhibit ideal device behavior at low bias (\(V_{DS}=0.1\) V). At high bias (\(V_{DS}<10\) V, \(L=30\) μm), however, the full gate device shows pronounced ambipolar conduction, unlike the partial gate case. Figure 4.3c illustrates the effect of source-drain bias and gate overlap (\(L_{ov}\)) on on/off ratio, where all measurements were performed on the same SWNT. The device with 5 μm gate overlap (i.e. the configuration used for TcEP) exhibits on/off ratios 2-3 orders of magnitude higher than the device with full overlap.
(L_w=30 μm). Figure 4.4d shows the ability of the partial gate configuration to maintain current levels several orders of magnitude lower than that of the full gate configuration, even for long bias durations (“off” state, V_{DS}=-40V, V_{GS}=+20V, 5 min, consistent with TcEP experiments).

4.6 SJEM Experiments

Figure 4.5a shows an SJEM image of an array of SWNTs (two terminal device, SiO_2 (200 nm) / Si substrate) covered with a 120 nm thick film of PMMA, collected at the condition of \( V(t) = V_{DS} \cos(2\pi f t) \) with \( V_{DS}=3V \) and \( f=30kHz \) and \( V_{GS}=0V \). Figure 4.5a shows the integrated expansion percentage (I.E.P.). To determine this quantity, we first located the maximum expansion along each measured cross-section perpendicular to the length of the SWNT. Next, we integrated these values along each SWNT, to get the integrated expansion (I.E.). The I.E.P. is the ratio of the I.E. to the sum of the I.E. for all three SWNTs, times 100%. Since the maximum expansion is proportional to the input power, the I.E.P. can be used to estimate the power input for each SWNT, from the measured total power into the device. Figure 4.5c shows a 3D rendering of the SJEM signal for the SWNT associated with Fig. 3.2b. Figure 4.5d shows a schematic of the SJEM measurement.

4.7 Temperature Distributions Associated with Joule Heating in Individual SWNTs

In this section, we describe procedures for determining the temperature distribution resulting from a SWNT embedded in a film of PMMA on SiO_2/Si substrate with power dissipation at the SWNT for an AC applied voltage. The temperature rise at the surface of the Tc-resist can be obtained by considering first the analytical solution for a disk heat source with radius \( r_0 \) at the interface between the Tc-resist and the SiO_2. Here, a cylindrical coordinate
system is set such that the origin is coincident with the center of the heat source as shown in Fig. 4.6a,b. The heat transfer governing equation temperature in cylindrical coordinate is

\[ \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} - \alpha \frac{\partial T}{\partial t} = 0 \]

where \( \alpha = \frac{k}{c\rho} \) is thermal diffusivity, \( k \) is thermal conductivity, \( \rho \) is density, and \( c \) is specific heat capacity. The subscripts 0, 1 and 2 denote \( T_{c-resist}, SiO_2 \) and \( Si \), respectively. Setting \( \theta = T - T_\infty \), where \( T_\infty \) is the remote temperature, the above equation is equivalent to

\[ \frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} + \frac{\partial^2 \theta}{\partial z^2} = \alpha \frac{\partial \theta}{\partial t} \]

The boundary conditions are

(1) \( z = -h_0 \) (top surface)

\[ -k_0 \frac{\partial \theta}{\partial z} \bigg|_{z=-h_0} = 0 \]

(2) \( z = 0 \)

\[ \theta_r = \theta_{r'}, -k_0 \frac{\partial \theta}{\partial z} \bigg|_{z=0'} = \begin{cases} Q_1 & 0 \leq r \leq r_0 \\ Q_{c1} & r_0 < r < +\infty \end{cases}, -k_1 \frac{\partial \theta}{\partial z} \bigg|_{z=0'} = \begin{cases} Q_2 & 0 \leq r \leq r_0 \\ Q_{c1} & r_0 < r < +\infty \end{cases} \]

where \( Q_1 \) and \( Q_2 \) satisfy \(-Q_1 + Q_2 = \frac{P}{\pi r_0^2}\), \( P \) is the total power of the disk.

(3) \( z = h_1 \)

\[ \theta_{r'} = \theta_{r'} \quad \text{and} \quad -k_1 \frac{\partial \theta}{\partial z} \bigg|_{z=h_1} = -k_2 \frac{\partial \theta}{\partial z} \bigg|_{z=h_1} \]
\( z = h_1 + h_2 \sim \infty \)

\[ \theta_{h_1+h_2} = 0 \quad (6) \]

For a voltage \( V(t) = V_0 \cos(\omega t) \) with angular frequency \( \omega = 2\pi f \), the Joule heating has angular frequency \( 2\omega \). The total power of the disk can then be obtained as

\[ P(t) = P_0 \left[ 1 + \cos(2\omega t) \right]/2, \]

which yields a constant temperature rise (DC component) due to \( P_0/2 \) and a time oscillating temperature rise (AC component) due to \( P_0 \cos(2\omega t)/2 \). It should be noted that the DC component of temperature rise can be easily obtained by setting \( \omega = 0 \) in the solution of AC component.

The time oscillating temperature rise (AC component) has the same frequency as the power density, i.e. \( \theta(r, z, t) = \theta(r, z) \exp(2\omega i) \). Therefore, we have

\[ \frac{\partial^2 \theta}{\partial r^2} + \frac{1}{r} \frac{\partial \theta}{\partial r} + \frac{\partial^2 \theta}{\partial z^2} - q^2 \theta = 0 \quad (7) \]

where \( q^2 = \frac{2\omega i}{\alpha} \) and \( \theta = \theta(r, z) \).

Equation (7) can be solved via the Hankel transform, for which the following transform pair of the first kind is applicable,

\[ \varphi(r, z) = \int_0^\infty \tilde{\varphi}(\xi, z) J_0(\xi r) \xi d\xi \]

\[ \tilde{\varphi}(\xi, z) = \int_0^\infty \varphi(r, z) J_0(\xi r) rd\xi \]

where \( \varphi(r, z) \) is the original function, \( \tilde{\varphi}(\xi, z) \) is the transform, and \( J_0 \) is the 0th order Bessel function of the first kind. Equation (7) then becomes
\[ \frac{d^2 \bar{\theta}}{dz^2} - (\xi^2 + q^2) \bar{\theta} = 0 \]  \hspace{1cm} (9)

Solving the above equation gives

\[ \bar{\theta} = A \exp(z\sqrt{\xi^2 + q_0^2}) + B \exp(-z\sqrt{\xi^2 + q_0^2}) \] \hspace{1cm} (10)

where $A$ and $B$ are two unknown functions to be determined according to boundary and continuity conditions. The temperature rise is then obtained by

\[ \theta = \int_0^\infty \left( A e^{-\xi z} + B e^{\xi z} \right) J_0(\xi r) \xi d\xi \] \hspace{1cm} (11)

Therefore, the temperature rise in Hankel space at each layer is obtained as

- **Tc-resist**: $\bar{\theta}_0(\xi, z) = A_0 \exp(z\sqrt{\xi^2 + q_0^2}) + B_0 \exp(-z\sqrt{\xi^2 + q_0^2})$

- **SiO2 layer**: $\bar{\theta}_1(\xi, z) = A_1 \exp(z\sqrt{\xi^2 + q_1^2}) + B_1 \exp(-z\sqrt{\xi^2 + q_1^2})$

- **Si layer**: $\bar{\theta}_2(\xi, z) = A_2 \exp(z\sqrt{\xi^2 + q_2^2}) + B_2 \exp(-z\sqrt{\xi^2 + q_2^2})$

With BCs (3)-(6) in Hankel space, we can obtain the temperature at each layer. For example, $A_0$ and $B_0$ are given by

\[
A_0 = \frac{\kappa + 1}{(1 - \kappa) \left[ 1 + \exp(-2h_0 \sqrt{\xi^2 + q_0^2}) \right] + (\kappa + 1) \frac{k_0 \sqrt{\xi^2 + q_0^2}}{k_1 \sqrt{\xi^2 + q_1^2}} \left[ 1 - \exp(-2h_0 \sqrt{\xi^2 + q_0^2}) \right]}
\]

\[
B_0 = A_0 \exp(-2h_0 \sqrt{\xi^2 + q_0^2})
\]

\hspace{1cm} (12)
\[ 1 - \frac{k_2}{k_1} \sqrt{\frac{x^2 + q_i^2}{\frac{x^2}{\kappa^2} + q_i^2}} \exp(-2h_0 \sqrt{\frac{x^2}{\kappa^2} + q_i^2}) \]

where \( \kappa = \frac{k_2}{k_1} \sqrt{\frac{x^2 + q_i^2}{\frac{x^2}{\kappa^2} + q_i^2}} \exp(-2h_0 \sqrt{\frac{x^2}{\kappa^2} + q_i^2}) \)

The temperature rise due to the disk heat source can be obtained by Eq. (11). For example, the temperature rise in the Tc-resist is obtained as

\[
\theta(r, z) = \int_0^\infty A_0 \left[ \exp(z \sqrt{\xi^2 + q_0^2}) + \exp(-z \sqrt{\xi^2 + q_0^2} - 2h_0 \sqrt{\xi^2 + q_0^2}) \right] J_0 (\xi r) \xi d\xi
\]

(13)

The surface temperature rise of the Tc-resist is then obtained by setting \( z = -h_0 \) as

\[
\theta(r) = \int_0^\infty 2A_0 \exp(-h_0 \sqrt{\xi^2 + q_0^2}) J_0 (\xi r) \xi d\xi
\]

(14)

As \( r_0 \to 0 \), we obtain the temperature rise due to a point heat source as

\[
\theta_p(r) = \frac{1}{4k_1 \pi} \int_0^\infty \frac{(\kappa + 1) J_0 (\xi r) \xi}{(1 - \kappa) \cosh(h_0 \sqrt{\xi^2 + q_0^2}) + (\kappa + 1) \frac{k_0 \sqrt{\xi^2 + q_0^2}}{k_1 \sqrt{\frac{x^2}{\kappa^2} + q_i^2}} \sinh(h_0 \sqrt{\frac{x^2}{\kappa^2} + q_i^2})} \cdot \frac{P_0}{\sqrt{\xi^2 + q_0^2}} d\xi
\]

(15)

For a point heat source at \( (0, \eta, 0) \) with heat generation \( P_0 = Q_0 \cdot d\eta \) and \( Q_0 \) as the power density, the integration of Eq. (15) with \( r = \sqrt{(\eta - y)^2 + x^2} \) gives the temperature rise at point \( (x, y) \) due to a line heat source as
\[ \theta(x, y) = \frac{1}{4k_t \pi} \int_{-L/2}^{L/2} d\eta \int_0^{\infty} \left( \kappa + 1 \right) J_0 \left( \xi \sqrt{(\eta - y)^2 + x^2} \right) \frac{Q_0}{\sqrt{\xi^2 + q_0^2}} \frac{1 - \kappa}{\kappa} \cosh(h_0 \sqrt{\xi^2 + q_0^2}) + \frac{(\kappa + 1)}{\kappa} \frac{k_t \sqrt{\xi^2 + q_0^2}}{k_f \sqrt{\xi^2 + q_f^2}} \sinh(h_0 \sqrt{\xi^2 + q_0^2}) \right) \cdot d\xi \]
where \(k_f\) and \(k_s\) are the thermal conductivity of Tc-resist and quartz, respectively and \(h_f\) is the thickness of Tc-resist.

A 3D finite element model was established to study the temperature distribution in the system and validate the analytical model. Eight-node, hexahedral brick elements in the finite element software ABAQUS are used to discretize the geometry. A volume heat source was applied on the SWNT. The zero heat flux boundary was applied at the top surface of the Tc-resist, and a constant temperature \(T_\infty\) is applied at the bottom of the quartz substrate. The finite element simulations agree well with analytical modeling as shown in Fig. 4.6c for the surface temperature of the Tc-resist with with \(k_0 = 0.2\,\text{W/m/K}, k_f = 6\,\text{W/m/K}, Q_o = 16.7\,\mu\text{W/\mu m}\) and \(L=30\,\mu\text{m}\).

### 4.8 Modeling of Thermocapillary Flow in TcEP

The viscous flow of Tc-resist is essentially unidirectional and the evolution of film thickness \(h(x,t)\) can be obtained from a lubrication equation

\[
\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left[ \frac{\tau h^2}{2\mu} + \frac{h^3}{3\mu} \frac{\partial}{\partial x} \left( \gamma \frac{\partial^2 h}{\partial x^2} \right) \right] = 0. \tag{19}
\]

where \(\gamma\) is the surface tension, which usually linearly depends on the temperature rise (i.e., \(\gamma = \gamma_0 - \gamma_1 \theta\)), \(\tau = \frac{\partial \gamma}{\partial T} \frac{\partial T}{\partial x}\) is the thermocapillary stress with \(T = T_\infty + \theta\), and \(\mu\) is viscosity. By introducing the following non-dimensional terms \(\bar{h} = h/h_f\), \(\bar{x} = x/h_f\), \(\bar{t} = \gamma_1 Q_o t / (\mu_o k_f h_f^2)\), \(\bar{\mu} = \mu/\mu_o\), \(\bar{\gamma} = k_f h_f \gamma / (Q_o \gamma_1)\), \(\bar{\tau} = \partial^2 \bar{h} / \partial \bar{x}^2\) and \(\bar{\theta} = k_f h_f \theta / Q_o\), Equation (19) can be written in non-dimensional form as
\[
\frac{\partial \bar{h}}{\partial t} + \frac{\partial}{\partial x} \left[ \frac{\tau \bar{h}^2}{2 \mu} + \frac{\bar{h}}{3 \mu} \frac{\partial}{\partial x} \left( \nabla \cdot \frac{\partial \bar{h}}{\partial x^2} \right) \right] = 0. \tag{20}
\]

The Fortran solver PDE_1D_MG can be used to solve for \( \bar{h} \).

4.9 Experimental and Theoretical Time Dependence of Trench Evolution in TcEP

The time dependence of trench evolution was studied for a small area (3x3 μm) within an array of SWNTs by collecting a sequence of AFM images (~30 s), for different durations of applied bias \( V_{DS} = 0.66 \text{ V/μm}, L = 30 \text{ μm}, 30 ^\circ \text{C background heating} \). During imaging no bias was applied, thereby leaving the trenches in fixed geometries for the duration of the measurement. In between images, biases were applied, driving trench formation for controlled durations (durations varied depending on accumulated duration ranging from 0.1 s for very short accumulated duration, <10 s, to 30 min for very long accumulated duration, 6-8 hrs). The total time of trench formation was taken to be the sum of the durations for all preceding experiments. Figure 4.7 shows representative images at various points in the evolution of trenches (Fig. 3.3c shows cropped images associated with the second trench from the left). At relatively short durations, trenches were shallow (< 1 nm deep) and characterized by slight ridges in the Tc-resist on each side of the SWNT, over time evolving into fully formed trenches, which grow and eventually (hours) began to interact with trenches from adjacent SWNTs, limiting further growth. Data associated with analysis of time dependence was restricted to durations where trenches were isolated from one another (<2 hr). For the purposes of establishing reliable measures of trench evolution, the trench width, \( W_{Tc} \), was defined as the width between the peak of the pile-up on either side of the trench (actual minimum widths, evaluated at the base of the Tc-resist, were much narrower). Analysis to determine the left and right side of the trench was
performed in MATLAB, and involved identifying the first location to the left and right side of the trench where the slope fell below a certain threshold, $5 \times 10^{-11}$. Figure 4.8a shows an AFM image for $t=600$ s with the identified left and right sides of the trench highlighted for the three central trenches. Figure 4.8b shows cross-sectional profiles associated with the central trench at various points in the trench evolution and the identified left and right positions. Figures 3.3f and 4.9a show the resulting experimentally extracted $W_{Tc}$. Smaller trenches ($W_{Tc} < 150$ nm, associated with $t < 10$ min), were less distinct, and identifying the left and right positions was more difficult. While values of $W_{Tc}$ were roughly accurate, there was significantly more error at shorter times than longer times. The short time values were not used for power law fitting (Fig 4.9a). Power law fitting was performed in data ranges where the standard deviation was $<10\%$ of $W_{Tc}$. (For data outside of this range, standard deviation was $W_{Tc} \sim 20$-50\% of $W_{Tc}$). The data fit well to a power law with exponent 0.25 (The value for the constant of proportionality, $A$, are shown). Figure 4.9b shows the predicted $W_{Tc}$ based on modeled trench profiles (peaks in $\bar{h}(x,\bar{t})$), which also fit well to a power law with exponent of 0.25 (The parameter $A$ depends on various Tc-resist properties, several of which are unknown). Figures 4.9c,d show the predicted $W_{Tc}$ for power densities varying from $8.3-33.3$ μW/μm for long durations and for durations that yield trench widths associated with those typical for TcEP. (Comparison to model can be difficult given the uncertainty in materials properties for the Tc-resist. Because $\bar{t}$ is normalized with respect to $\mu$ and $\gamma$, which are unknown, it is not possible to compare directly to $t$. Nevertheless, the computed $W_{Tc}$ is only normalized by $h_0$, so it is meaningful to compare modeled $\bar{t}$ to ranges of experimental $t$ that yield trenches of similar size to those measured experimentally). For long times, $W_{Tc}$ varies with power density. At durations associated with experimental conditions, however, almost no variation is predicted. This relative insensitivity to power is consistent with
experimental observation (Fig. 3.2e,f), where only~20% variations in $W_{Tc}$ are typically observed. Such variations likely result from local changes in film viscosity associated with heating, or other effects not explicitly included in the model.

4.10 Thermocapillary Flows in Tc-resist, Studied by Heated AFM Tips with Integrated Temperature Sensors

Heated atomic force microscope (AFM) tips with known temperatures contacted with the Tc-resist layer for various times, and with various applied powers, allow study of the effects of thermocapillary flow in a nanoscale system where temperature and other parameters are controlled (and known) more accurately than the case for SWNTs. The heated tip (radius <100 nm) was fabricated from doped single crystal silicon, and is capable of reaching temperatures of 1000 °C with a temperature calibration to within 5 °C for this entire range. Previous studies of viscous mass flow from a heated tip to a substrate revealed thermocapillarity to be an important driver of flow. Figure 4.10 shows Tc-resist layer deformation induced by tip heating for tip-substrate temperature differences between 5 – 45 °C and dwell times between 0.1 – 300 s on both an unheated Tc-resist layer and a Tc-resist layer heated to 50 °C. The tip dwelled on the surface with tip forces below 20 nN and did not deform the surface when unheated. The results show that significant material flows radially away from the heated tip for Tc-resist layer temperatures far below the sublimation temperature, consistent with thermocapillary stresses induced by the temperature gradient around the tip.

4.11 Pulsed Heating in TcEP for Large Scale Arrays of SWNTs

For arrays that contain large numbers of SWNTs (either at high densities or over large areas) the coupled heating of many SWNT leads to bulk, and sometimes large, increases in
temperature. These effects can yield thermocapillary flow on larger length scales and in ways that are difficult to confine to the positions of the SWNTs (Fig. 4.11). Pulsed bias conditions (~1-10 μs) can avoid these cumulative effects, to yield localized heating and thereby preserve well-behaved trenches even with large arrays of SWNTs and/or relatively high densities (up to 3 SWNT/μm studied here). Figure 4.11, shows the resulting trenches for a localized region within a large area high density array (30 μm x 1 mm, 2-3 SWNT/μm) for increasing duty cycles (10 to 100%) with a fixed pulse duration (10 μs). These data clearly show the gradual transition from narrow, well defined trenches associated with individual SWNTs to uncontrolled flow not correlated to SWNTs.

4.12 Tc-resist Material Selection

There are numerous characteristics that are critical for an effective Tc-resist material. Basic requirements are that the material can be easily deposited in thin film configurations, where vacuum deposition is preferable to spin coating, since it easily yields uniform film thickness even in regions near the partial gate electrode structures, where substrate topography is highly nonuniform. The films must afford good coverage and adhesion to both the SWNT and the quartz substrate, and at the same time be sufficiently impermeable to O₂/CF₄ plasma to act as an effective etch resist. The unique chemistry of the Tc-resist material studied here combines hydroxyl and phenyl moieties which provide compatibility with both SWNT and oxide substrates. It is critical for films to exist in an amorphous phase, to avoid spatial nonuniformities in thermal properties (thermal conductivity, k), viscous flow properties (temperature coefficient of surface tension, γ₁, and viscosity, μ) and thickness that can be associated with crystalline grains. Figure 4.12a,b,c shows AFM associated with trench formation experiments with arrays of SWNTs and Tc-resists consisting of thin films of paraffin, TCNQ, and pentacene (similar
results were achieved for TCTA and F4-TCNQ). All of these materials show features that roughly correlate to underlying SWNT heaters, but showed massive variations in resulting trenches over the area of the film. Films of TAZ and anthracene (deposited at -80 °C) yielded amorphous films, but, over the time scales associated with experiments and characterization, exhibited spontaneous crystallization. Other materials, such as polystyrene (MW=288,000, Fig. 4.12d) or Alq3 provided high quality amorphous films, but significantly higher power densities (and/or higher background heating, $T_\infty > 140$ °C) were required to yield trenches. (In the case of Alq3, crystallization occurred at lower temperatures than those required for trenches to be observed, in reasonable experimental time scales). These power densities (or background heating) lead to bias requirements and/or operating conditions in which non-ideal device behaviors (e.g. non-negligible current through the s-SWNTs) limit the selectivity of the TcEP process. Models of thermocapillary flow suggest that such behaviors are due to either low temperature coefficients of surface tension or high viscosities. While both parameters play an important role in the flow (and $\gamma_f$ also plays a role in the trench profile), most materials exhibit $\gamma_f$ between ~0.05 and ~0.15 mJ/m$^2$/°C, while viscosities can vary by many orders of magnitude. It is likely, then, that viscosity is the most significant parameter that determines whether materials yield trenches in experimentally practical time scales and with low power levels, without significant background heating. While the Tc-resist demonstrated here meets all of these criteria, advances could be obtained through the development of materials with similar properties but also with the ability for use at smaller thicknesses (e.g. 5-10 nm, rather than 25 nm). Reductions in thickness enable decreases in $W_{Tc}$ (linearly with $h_f$) which, in turn, could allow application to arrays of SWNTs with high densities.
4.13 Processes Defined by Critical Temperatures

The unique scaling (particularly power invariance) associated with thermocapillary flow is critical to the success of TcEP, because it allows uniform trenches in arrays of SWNT that incorporate significant variations in power densities among the various SWNTs. Although it is possible to envision approaches like TcEP but which rely on processes such as sublimation or ablation, their robust operation is limited by the existence of a critical temperature, \( T_C \). In such cases, at temperatures below \( T_C \), the resist will remain, while at temperatures above \( T_C \), the film will be removed. Thermal models can provide key insights into the scaling of this type of process. Figure 4.13a,b show temperature profiles and thermal gradients for a range of power densities similar to those measured experimentally. Both peak power and peak gradient scale linearly with power. A width associated with a process that relies on a critical temperature, \( W_C \), can be determined (Fig. 4.13a). Figures 4.13c,d show the predicted scaling for processes associated with critical temperatures of 2-10 °C. It reveals that these processes yield no trench until a certain power density is reached. Afterward, the width increases dramatically with increasing power, to widths that would expose other SWNT in arrays of densities >0.1 SWNT/μm. This type of scaling is incompatible with desired operation. For higher \( T_C \) the range of powers that yield practical trench widths (several hundred nm) becomes larger. Here, the required power density to initiate trenches grows dramatically, which is also highly undesirable.

4.14 Effects of Trench Formation in Neighboring SWNTs

For very high SWNT densities, non-ideal behavior in TcEP can occur if a trench associated with an m-SWNT exposes an s-SWNT in close proximity. The trench width provides an indicator for the density at which this type of behavior can be expected. In particular, for an
array of SWNTs with regular spacing, the maximum density is defined roughly by the average trench width (trench width measured at the base of the Tc-resist ~100 nm, where $W_{Tc}$ is ~250 nm). We note, however, that thermocapillary flow can be altered as neighboring trenches approach one another. At long times the pileup from two adjacent trenches coalesces, creating a narrow strip of Tc-resist in between them. It is unclear from the simple models here, which apply to isolated SWNT, how close the SWNTs can be before their trenches merge. As a result, the minimum spacing between trenches where Tc-resist remains in between them provides the best indicator of the maximum density that can be accommodated in TcEP, as implemented here. AFM measurements of trench formation in arrays with locally high densities suggest that neighboring trenches can be as close as 250 nm while still showing well-defined Tc-resist in between. Figure 4.14 shows an AFM, cross-sectional height profile, and associated 3D renderings of such trenches. Here, isolated trenches are observed along the entire lengths of the trenches (~8 μm).

4.15 References


4.16 Figures

5 min, 60 °C background, $V_{GS} = +20$ V (off state), Various $V_{DS}$

Figure 4.1 Critical power for trench formation. Summary of results on experimental investigations of trench formation (5 min, 60 °C background, $V_{GS} = +20$ V (off state), Various $V_{DS}$ in devices with single or several SWNT, in which an individual SWNT contributed a majority of the current. The findings define the critical power density to form trenches. All experiments were performed with s-SWNT in their “off” state (+20 $V_G$). (a) Scatter plot of device-level power density associated with the experiments. All devices with power density below 3.3 $\mu$W/µm show no trenches (blue), all devices with power density above 10 $\mu$W/µm show complete trenches along the entirety of their length (red), while those with intermediate powers show trenches along part of their length (yellow).
**Figure 4.1 continued.** Here, local variations in resistance along the length of the SWNT yield powers sufficient for trench formation in some, but not all regions of the SWNT. (b) The same set of experiments, organized by source-drain bias and SWNT electronic type. Although there is a large variation in the power associated with various SWNT at a given bias condition, for optimized conditions (-1.33 and -1.66 V/µm) all s-SWNT exhibit no trenches, while all m-SWNT exhibit complete trenches along their entire length. (c) Representative AFM images for: no trench (left), partial trench (middle), and complete trench (right) formation.
Figure 4.2 Tc-resist characterization. (a) Chemical structure for Tc-resist. (b) AFM of a pristine film deposited by thermal evaporation (25 nm, ~1Å/s) showing a very smooth surface (2-3 Å RMS roughness, similar to underlying Si substrate). (c) DSC of Tc-resist showing specific heat (~1.5 J/C/cm³), melting temperature (~225 °C), recrystallization (~150 °C), and glass transition (~95 °C) for a bulk sample. (d) Thermoreflectance for a 300 nm thick film of Tc-resist. Fitting yields thermal conductivities of ~0.2 W/m/K.
Figure 4.3 SWNT resistivity data. (a) Extracted average resistivity for m-SWNTs and s-SWNTs based on sorted small area arrays. Average resistivity for each of 37 devices based on device resistance changes before and after TcEP and the number of SWNTs removed and remaining (based on AFM). (b) Typical I-V for an array before and after TcEP showing the relative conductance attributed to both m-SWNT and s-SWNT. (c,d) Histograms showing distributions of individual SWNT resistivities for two data sets, one based on back-gated devices on SiO$_2$/Si and the other based on top-gated devices with a gate dielectric of SOG/HfO$_2$. Distributions representative of previously published results on arrays of SWNT.
Figure 4.4 Effect of partial gate transistor geometry. Electrical characterization of an individual SWNT device with varying gate overlap. Transfer characteristics for different drain voltages ($V_{DS}=-0.1, -20, -40$ V) for the case of (a) partial gate and (b) full gate configurations. (c) $I_{on}/I_{off}$ dependence on gate overlap ($L_{ov}$) ranging from 5 to 30 µm and (d) drain current associated with devices held in their off state ($V_{GS}=+20$ V) for extended durations, for partial gate and full covered configurations.
Figure 4.5 Summary of SJEM measurements. (a) Full SJEM image for an array of 3 SWNTs. The relative integrated intensity for each SWNT is indicated. This relative intensity is used to calculate the relative proportion of the total device power density associated with each SWNT. (b) Transfer characteristic of a device with an array of 3 SWNTs. (c) SJEM image for a SWNT used for validation of analytical temperature models (Fig. 2c). (d) Schematic illustration of SJEM measurements.
Figure 4.6 Thermal modeling geometry. (a) Cross-sectional schematic of the film and substrate geometry associated with thermal modeling, with axes defined. (b) Modeling axes defined relative to the position of the SWNT. (c) Tc-resist surface temperature distribution for the case of a heated SWNT on a quartz substrate (16.6 μW/μm).
Figure 4.7 Time dependent trench formation study. 3x3 μm AFM images associated with in-situ measurement of trench formation. Brief intervals of bias were applied and the associated topography was measured (30 s scans) in between each interval. These images are associated with various total accumulated bias durations as trenches evolve.
Figure 4.8 Details of trench width identification. (a) Representative image of trench formation. Lines showing the position identified as the right and left trench edge. (b) Representative cross-sectional height profiles at various points in trench evolution. For the purposes of establishing reliable methods of consistently identifying trench width that are independent of AFM tip condition and can yield comparison to features easily identified by thermocapillary flow modeling, the trench edges were associated with the peaks of the pileup on the trench edge. As is evident from the cross-section profiles, that width of the trench at the base is substantially narrower than these values. AFM tip artifacts make precise measurement of this inner width difficult.
Figure 4.9 Time dependence of trench width. (a) Experimental results showing power law time dependence, with $t^{0.25}$ scaling, for the width. Trenches associated with different SWNTs have slightly different prefactors, most likely associated with slight differences in relative power densities. (b) Modeling showing similar $t^{0.25}$ dependence, thus indicating that the model for Tc-flow accurately captures the fundamental scaling of trench formation. (c,d) Time dependence of width for various powers over long and short time scales respectively. For short time scales, where trench widths are comparable to those in TcEP, the width only depends weakly on the power.
Figure 4.10 Thermocapillary flows in Tc-resist studied with calibrated, heated AFM tips. AFM images of a series of arrays of dots patterned in films of Tc-resist, created by contact of heated AFM tips for a variety of temperature differences (tip to substrate) and contact durations (indicated in first frame) at both room temperature and 60 °C. General behavior is consistent with that observed for SWNT Joule heating. In particular, features form in the Tc-resist even at low temperature rises. Feature sizes increase with time.
Figure 4.11 Pulsed biases for forming trenches in large and/or high density arrays of SWNTs. AFM trenches formed in Tc-resist for an array with 2-3 SWNT/µm associated with pulsed heating with increasing duty cycle ($V_{DS} = -40V$ peak amplitude, period= 10 µs, duration= 1-10 µs, $V_{GS} = +20V$ DC, 60 sec total stress duration, 50 °C background heating). For 10% duty cycle clearly defined trenches are observed. As the duty cycle increases, trenches become less clearly defined and flow is observed that does not correlate to the underlying SWNT positions. This results from delocalized heating associated with parallel operation in many SWNT. Pulsed heating aids in localizing the flows needed for proper operation in TcEP.
Figure 4.12 Behaviors in other candidate materials for Tc-resists. AFM images of trenches formed for (a) paraffin, (b) TCNQ, and (c) pentacene. Some trenches are observed, but with non-uniform widths. For these materials, such behaviors can be attributed to their morphology. Other materials explored, such as polystyrene (d) failed as Tc-resists due to inability to form trenches at sufficiently low powers (likely due to high viscosity or low temperature coefficient of surface tension) and/or insufficient etch resistance.
Figure 4.13 Theoretical trench width for processes based on critical temperatures. (a,b) Temperature profiles and gradients predicted by analytical thermal models for a variety of powers. Processes such as sublimation or ablation have a critical temperature associated with them such that all material at or above this temperature is removed and all below the critical temperature is preserved. (c,d) Power dependence of predicted trench width associated with processes with critical temperatures ranging from 2-10 °C. Processes with higher critical temperature should show similar scaling but with higher power density required to yield trenches (unsuitable for TcEP). This type of scaling is not ideal for TcEP, since at conditions sufficient to yield trenches in the least conductive m-SWNT, the most conductive SWNTs would exhibit very wide trenches (several µm), thereby exposing neighboring SWNTs.
Figure 4.14 Trenches in cases with neighboring SWNTs. AFM images associated with two distinct trenches that form from heating in neighboring SWNTs. Despite their close proximity (250 nm) two distinct trenches form along the lengths of the SWNTs (~10 µm).
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Table 4.1. Thermal and Mechanical parameters used in analytical and FE models
CHAPTER 5

DEVICE DEMONSTRATIONS BASED ON ARRAYS OF SWNTS


5.1 Introduction

Aligned arrays of SWNT offer the most effective way to incorporate the excellent electronic properties of SWNT into practical electronic device configurations. Chapters 2-4 described techniques to achieve aligned arrays of high purity s-SWNT based on CVD on single crystalline quartz substrates and subsequent TcEP. Here we demonstrate the practical use of these arrays for a variety of device applications. One demonstration consists of submicron transistors based on unpurified arrays of SWNT (the implications of m-SWNT will be discussed). The second consist of basic device demonstrations utilizing arrays of SWNT purified by TcEP.

5.2 Submicron Transistors Based on Aligned Arrays of SWNTs for RF

Fundamental experimental\textsuperscript{1} and theoretical studies\textsuperscript{2,3} suggest that SWNTs can respond on picosecond time scales, corresponding to frequencies approaching the terahertz regime.
Transistors that exploit the small capacitances\(^4\) (~100 aF/\(\mu\)m), large mobilities\(^5 \sim 8\) (~10\(^4\) cm\(^2\)/Vs), and high degree of linearity\(^9\) of SWNTs to achieve amplifiers\(^10\), oscillators\(^11\), circuits\(^12, 13\) and systems\(^14\) with operating speeds in this range are of considerable interest. Evaluating the scattering parameters (S-parameters) provides the most established and accepted procedure for determining the frequency responses in individual transistors. For devices that use single SWNTs, such measurements are confounded by parasitic capacitances and large impedance mismatches between the instrumentation and the devices. De-embedding and other procedures can, in principle, minimize the effects of parasitics but only with substantial uncertainties, mainly because the capacitances of the SWNTs are orders of magnitude smaller than the parasitics\(^15 \sim 19\).

The use of multiple SWNTs deposited from solution in random or partially aligned configurations\(^15, 20\) can reduce some of these problems, but the low output resistances and limited switching capabilities of reported devices (due, presumably, to a preponderance of metallic SWNTs in the channel) are undesirable for measurements and practical devices\(^21, 22\). Length scaling of properties has not been reported for either type of device. Here we present systematic studies of RF transistors that each incorporates large numbers (i.e. hundreds) of perfectly aligned, parallel SWNTs. Due to their reduced contribution from parasitic capacitances for practical channel widths (>\(\mu\)m) and dramatically improved impedance match to common measurement systems, these devices represent an attractive approach to SWNT RF electronics. Additionally, the comparatively high level of reproducibility in the device properties, the large transconductances and low impedances allow comprehensive evaluation of their modes of operation, though some degree of uncertainty remains due to variations in nanotube density, distributions of nanotube diameters and relative populations of semiconducting and metallic
nanotubes. The results establish quantitatively accurate, and predictive, small signal RF device models that provide guidelines for implementation of SWNTs in high frequency electronics.

Figure 5.1a shows an optical micrograph of a characteristic device on a quartz substrate, which involves hundreds of perfectly aligned, linear arrays of SWNTs (at densities of between 2 and 5 SWNTs/µm) grown by chemical vapor deposition (CVD)\(^{23-25}\). The device layout consists of two, separately fabricated parts: the probing pads and the active device. The active region was defined first. It employs a double channel configuration in which two gate electrodes and two source electrodes surround a common drain electrode. Fabrication involved two electron beam lithography (Raith, eLine) processes to define the source/drain and the gate levels, with accurate registration to maximize the width of the gate and to minimize the capacitances associated with overlap between the source/drain and the gate. A layer of HfO\(_2\) (50 nm) deposited by electron beam evaporation (Temescal CV-8) served as the gate dielectric. Photolithography defined comparatively large probing pads that provided electrical contact the smaller features of the active region. The configuration of the pads (3nm Ti:100nm Au), as defined by photolithography, matches that of conventional ground-signal-ground (GSG) microwave probes (150 µm pitch). Figures 5.1a and 5.1b present an optical micrograph of a representative device and a cross sectional schematic illustration, respectively. Arrays of devices formed in this manner had channel lengths \(L_g\) between 900 nm and 300 nm and channel widths \(W\) between 100 µm and 25 µm. The double channel geometry means that the total device width used for calculations is twice \(W\). For the remainder of the text, \(W\) will be used for the purposes of discussion. DC performance was evaluated using conventional setups (Agilent E5270B Precision Measurement Mainframe. The source monitor units were connected through two Agilent 11612B bias networks to a pair of 150 µm pitch Picoprobe microwave probes, just prior
to high frequency measurements. Figure 5.1d and 5.1e show transfer and output characteristics of a typical device ($L_g = 700$ nm; $W = 100$ µm; 5 SWNT/um), respectively. The devices show p channel behavior, with a moderate degree of ambipolar operation as is often observed with top gated SWNT transistors, either in array or single tube formats. For the device of figure 5.1, the on state current is $\sim 8.5$ mA at a drain bias ($V_d$) of -1 V. The peak transconductance ($g_m$) is $\sim 5$ mS (25 mS/mm of channel width), at a drain bias of -1 V and gate bias ($V_g$) of 0 V. For the same bias, the output resistance, $R_o$, is $\sim 520$ Ω, corresponding to a gain ($G=R_o g_m$) of $\sim 2.6$. In all cases, the ratio of the on state to off state current is close to three, due to the substantial (1/3) population of metallic nanotubes.

To determine the high frequency behavior, we measured the S-parameters directly, using standard procedures with a vector network analyzer over a frequency range of 0.5GHz to 50 GHz (Agilent 8364A). Calibration was performed to the probe-tips using off-wafer short-open-load-through (SOLT) standards on a GGB Industries CS-5 calibration substrate. Figure 5.2a shows the S-parameters for the device presented in Figures 5.1d and 5.1e. Figure 5.2b presents current gain ($H_{21}$), maximum available gain (MAG) and unilateral power gain ($U$), all derived from the S-parameters at a drain bias of -1 V and gate bias of 0 V. These results indicate unity-current-gain frequency ($f_t$) and unity-power gain frequency ($f_{max}$) of 5 GHz and 9 GHz, respectively. $f_t$ corresponds to the frequency for which the drain and gate current are equal, thus their ratio is unity. It is the frequency where the current gain, $H_{21}$, crosses the 0 dB line. $f_{max}$ is the maximum frequency of oscillation and it is determined by extracting Mason's Invariant (U) to 0 dB in a manner similar to that used for $f_t$. Figure 5.2c presents the dependence of $f_t$ and $f_{max}$ on drain bias. With increasing negative bias (-0.5 to -0.9 V), both $f_t$ and $f_{max}$ increase linearly, until they saturate at a drain bias of $\sim$ -1 V, which corresponds to an electric field of $\sim 5$ kV/cm. This electric field
approaches that needed to saturate the carrier velocity\textsuperscript{27}. Figure 5.2d presents the dependence of $f_t$ and $f_{\text{max}}$ on gate bias. Both $f_t$ and $f_{\text{max}}$ reach maximum values near $V_g \sim 0$ V, coinciding with the peak in $g_m$ (Figure 5.2e, from DC measurements) as expected. If we assume that

$$f_t \approx \frac{g_m}{2\pi(C_{gs} + C_{gd})},$$

where $C_{gs}$ and $C_{gd}$ are the capacitance between the gate and source electrodes and the gate and drain electrodes, respectively,\textsuperscript{6,19} then we estimate that $C_{gs} + C_{gd} \sim 171$ fF at the point of maximum $g_m$. This expression is reasonable in the case where parasitic resistances are small relative to output resistance, which is the case (shown subsequently) for these devices.

Scaling studies provide additional information. Figures 5.3a and 5.3b show the dependence of $f_{\text{max}}$ and $f_t$, respectively, on $L_g$ for two different device sets with average tube densities of \(~2\) SWNT/μm and 5 SWNT/μm and $W = 100$ μm. Both $f_{\text{max}}$ and $f_t$ increase with decreasing $L_g$, qualitatively consistent with expectation. The precise form of the scaling with channel length cannot be determined conclusively from these data. Some insights can, however, be obtained by noting first that the transconductances determined from DC measurements (Figure 5.2e) as well as those extracted through analysis of RF data (as described subsequently) yield similar values, with only a weak dependence on $L_g$, possibly due to the combined effects of contact resistance, near ballistic transport and systematic shifts in threshold voltage that we observed to increasingly positive values with decreasing channel length. As a result, one can conclude that for these devices, increases in operating frequency with decreasing $L_g$ result mainly from decreases in gate capacitances, $C_{gs}$ and $C_{gd}$, rather than increases in $g_m$, as is confirmed by the RF device analysis presented next. The scaling with $W$ is as expected: $g_m$, $C_{gs}$ and $C_{gd}$ all increase roughly linearly with increasing $W$, thereby yielding values of $f_t$ that are independent of $W$, as shown in Figure 5.3c for devices with $L_g \sim 700$ nm and a density of \(~2\) SWNT/μm. Some
additional insights into scaling and capacitance can be obtained by examining the dependence of \( f_t \) on \( g_m \), as shown in Figure 5.3d, derived from data collected at various \( V_g \) (Figure 5.2d and 5.2e). The approximate linear scaling that is observed over certain regions is consistent with values of \( C_{gs} \) and \( C_{gd} \) that do not vary strongly with \( V_g \), thereby suggesting a relatively small contribution of the semiconducting tubes to the overall gate capacitance, as is confirmed through analysis described in the following.

5.2.1 Small Signal Modeling and Scaling

To understand more fully the nature of device operation, we used hybrid-pi models, common for two-port small-signal response in conventional in transistors and circuit modeling, in which the behavior around a bias point is analyzed in the context of an equivalent circuit with linear physical quantities (such as capacitance, inductance and resistance). For sufficiently small signal variations, the response of the circuit is assumed to be linear with a behavior consistent with this model. The main parameters for the model, which was implemented with commercial software tools designed for this purpose (Agilent Advanced Design System), are the output resistance \( (R_o) \), the transconductance \( (g_m) \), the inductances \( (L') \) and resistances \( (R) \) of each of the metal electrodes (i.e. \( L'_g \), \( R_g \), \( L'_d \), \( R_d \), \( L'_s \), and \( R_s \), where subscripts \( g \), \( d \) and \( s \) refer to gate, drain and source, respectively), and the capacitances between gate-drain \( (C_{gd}) \), gate-source \( (C_{gs}) \), and drain-source \( (C_{ds}) \). \( L'_s \) is also set to zero due to the minimal inductance expected based on the layout of the source electrode. The remaining parameters and their topology within the model are shown in Figure 5.4a. The modulation of the semiconducting tubes by the gate is represented by a voltage-controlled current source located between the source and drain.

In principle, the parameters extracted from analysis of such a model can provide physically meaningful characteristics of the devices. The relatively large number of variables
and the complex topology of the error surface associated with the fitting process, however, create difficulties. To reduce the number of free variables, we performed measurements on test structures with geometries exactly the same as those of the devices but without the SWNTs and used techniques to constrain other parameters of the model. The test structures, which we refer to as ‘open’ devices, were evaluated using the same frequency dependent measurements as the active devices, and with similar models, for the purpose of de-embedding and to evaluate the parasitic capacitances due only to the electrode geometry. An optimized fit of the data to a somewhat simpler model (8 free variables), shows good agreement, up to 20 GHz. The resulting parameters (Table 5.1) provide information useful for fitting of data from the active devices. In particular, we can use the values of $R_s$, $R_d$, $R_g$, $L'_d$, and $L'_g$ determined from the open devices for modeling the active devices. (The resistances are within a factor of three of values calculated using the electrode geometries and bulk resistivities\textsuperscript{28}; table S1) Although the capacitances from the ‘open’ devices cannot be used in a similar manner, due to the absence of contributions from the SWNTs, they can yield insights into the meaning of these quantities from the active device modeling, as described subsequently.

Further constraints can be imposed on the active device variables. For example, $C_{gd}$ can be obtained from the single-pole roll off of $S_{12}$ (Figure 5.4d) with decreasing frequency. At low frequencies $C_{gd}$ is the dominant element determining reverse feedback through the transistor; $C_{gd}$ is manually adjusted to make the modeled and measured $S_{12}$ curves coincide at 200 MHz. The output resistance was set to the DC value, $R_o=520 \ \Omega$. Collectively, these considerations allow for a reduction of the fitting variables from 10 to 3, by fixing $R_s$, $R_d$, $R_g$, $R_o$, $L'_d$, $L'_g$ and $C_{gd}$. We found that the three remaining parameters could be determined reliably by fitting, independent of
starting values to within a few fF ($C_{gs}$ and $C_{ds}$) and tenths of mS ($g_m$). For the final optimization, the value of $C_{gd}$ was adjusted slightly following fitting to improve the overall fit.

The final optimization yielded good fits to $S$-parameter data (Figure 5.4b and 5.4d) measured from the device discussed in Figures 5.1 and 5.2 over two decades of frequency, up to 50 GHz. The maximum available gain, which is derived from these $S$-parameters (Figure 5.4c), also shows excellent agreement. The values found for the optimization parameters appear in Table 5.1. As mentioned earlier, $g_m$ extracted from RF analysis correlates well to DC values (Figure 5.2e). The same model was used to evaluate the channel length and channel width scaling of parameters for the devices presented in figure 5.3 with 2 SWNT/μm. In all cases, values of $g_m$ extracted in this manner correspond well to those determined from DC measurements, indicating no systematic variation with channel length. The capacitances determined for the active device are similar to those for the open device (Table 5.1), consistent with the conclusion that contributions due to semiconducting nanotubes are relatively small compared to parasitics, as also suggested by the relationship of $f_t$ and $g_m$ (Figure 5.3d). The value of $C_{gs}+C_{gd}$ from this RF analysis yields ~135 fF, which is comparable to that determined from direct measurements of $f_t$ and $g_m$ and an approximate relationship between these quantities, as discussed previously. $C_{gs}$ and $C_{gd}$ were also found to scale with increasing channel length and width, as is expected with an increasing gate area. As mentioned previously, this scaling is most like responsible for the trends observed in $f_t$.

To gain additional insights into the capacitances, we examined their dependence on $V_d^{29}$. Because the devices studied here operate in depletion-mode, at small source/drain bias (e.g. -0.5 V < $V_d$ < 0 V), the devices are in the linear response regime, such that we can assume that the charge distributions on the SWNTs are spatially symmetric. Figure 5.5a shows the output
response due only to semiconducting SWNTs, generated by subtracting the current due to metallic SWNTs (i.e. the device in its off state). At high bias (e.g. -1.5 V < V_d < -0.5 V), the devices are in saturation and the charge distributions are asymmetric (Figure 5.5). Figure 5.5b shows C_{gs} and C_{gd}, extracted via fitting of RF data for the device described in Figures 5.1 and 5.2, as described above, as a function of V_d. In the linear region, C_{gs} and C_{gd} have similar values, which we write as C_p+C_{ox}/2 where C_{ox} is the capacitance contribution associated with the coupling of the semiconducting tubes to the gate electrode, and C_p is associated with all other contributions (i.e. metallic tubes, fringing fields, overlaps, etc). In saturation, as the drain voltage is decreased, C_{gd} decreases, due to the asymmetry of the charge distribution; the value of C_{gd} in this regime gives C_p directly\(^{29}\). By similar reasoning, C_{gs} increases to 2C_{ox}/3+C_p in saturation. This analysis yields the parasitic capacitance, C_p~51 fF and the gate oxide capacitance C_{ox}~22 fF. Calculations that include full effects of fringing fields and screening of tubes in the arrays and the quantum capacitances, with device dimensions reported previously and a dielectric constant of ~14 for the HfO_2, yield a computed C_{ox} of ~30-40 fF for tube densities of 4-5 SWNTs/\mu m, with negligible effects of non-uniform tube-tube spacings in the array. The quantity C_p has contributions from fringing fields between the metal electrodes (C_f) and from the metallic SWNTs (C_m), the latter of which we consider also as parasitic because these tubes contribute capacitance without contributing to g_m. If we assume a 2:1 ratio of semiconducting to metallic tubes\(^{30}\), then the parasitic capacitance of the metallic tubes is C_m~10 fF, which yields C_f~40 fF. This value of fringing capacitance is in the same range as values obtained by finite element modeling (~55 fF). These parameters, together with the carrier velocity (v_s), determine the intrinsic switching time of the device. For a short channel device, the carrier velocity can be written as \( v_s = \frac{g_m L_g}{C_{ox}} \). With parameters outlined above, this equation
yields $v_s \sim 1.2 \times 10^7$ cm/sec, which agrees well with previous reported values ($\sim 2 \times 10^7$ cm/sec)$^{27}$. The intrinsic cut-off frequency, can be evaluated by considering a device that is free of parasitics, such that $f_i = \frac{g_m}{2\pi C_{ox}}$. Here we find the intrinsic cut-off frequency to be $\sim 30$ GHz, which is at least 6 times higher than the measured devices, all of which are dominated by parasitics. This metric defines performance expected for a single nanotube transistor free of parasitics. In addition, it represents the upper limit achievable with array based SWNT transistors with densities sufficiently high to eliminate the significance of the parasitics and with metallic SWNTs removed, thereby eliminating their contributions to capacitance.

In summary, we constructed high speed nanotube transistors from aligned arrays of hundreds of parallel nanotubes and assessed their performance by evaluating scattering parameters in the RF range. Interpretation of the results relied on small signal modeling of the RF response and on scaling analysis of properties in the DC and RF range. The results indicate that the gate capacitances, including significant contributions from parasitics for the devices examined here, have a dominant effect on the RF behavior and on $f_i$ and $f_{max}$ in particular. The relative contributions to this capacitance by semiconducting and metallic nanotubes as well as fringing fields between device electrodes were assessed. Performance not limited by parasitics (not including those associated with metallic tubes) corresponds to the case where $C_{ox} >> C_f$. Devices that involve sufficiently high densities of SWNTs can reach this regime. Further improvements ($\sim 1.5x$ for the case when $C_f$ is small) are possible by eliminating the metallic tubes and, therefore, their contribution to capacitance. These two conclusions provide goals for future work on growth and purification of arrays of SWNTs, for applications in high speed electronics.

5.3 Transistors Based on TcEP Purified Arrays of SWNTs
Because TcEP operates on entire arrays SWNTs, rather than on specific device geometries, it allows integration of s-SWNT arrays into nearly any type of component or circuit layout. Short channel (~800 nm) devices, formed with arrays of s-SWNTs, provide a demonstration; Figs. 5a,b show the design and a micrograph of an example device. Figure 5c presents the electrical properties, which exhibit levels of conductance that are in an expected range, limited by contact resistance at these scaled dimensions (~10 SWNT following TcEP, for the diameters here, contact resistance should be significant). Short channel devices of this type are difficult or impossible to fabricate reliably using a traditional method to eliminate the role of m-SWNTs, such as electrical breakdown, for two reasons: (1) heat sinking at electrode contacts progressively drive required powers to levels that reduce selectivity and lead to biases that can cause electrical breakdown in the necessarily thin gate dielectrics and (2) arrays of SWNT processed by breakdown in large device geometries lead to small discontinuities in the m-SWNTs at positions that cannot be aligned, in determinate fashion, with the channels of subsequently fabricated devices. A simple logic gate, consisting of two transistors using arrays of s-SWNTs, provides a final example of the utility of TcEP, as illustrated in Fig. 5d,e. Figure 5f shows the voltage transfer characteristics and gain associated with this p-type inverter. The peak gain was ~4, consistent with conventional diode-load inverter designs.

5.3.1 Interconnected arrays of SWNT for large area TcEP

For applications where the collections of devices in a target application are known roughly, then it is practical to perform TcEP in local patches, as part of an interconnected array of electrodes. Figure 5.7a shows five 1x5 sets of SWNT processed by TcEP in this manner. Figure 5.7b,c show the transfer characteristics for one of the arrays before and after TcEP and the characteristics for all five devices after TcEP. Table 5.2 summarizes the results for all five
arrays. For each array, after removing interconnects (lithography and etching), all of the devices (25 total) showed high on/off ratio ($> 1 \times 10^3$). This result demonstrates the effectiveness of performing TcEP over large areas using this type of interconnection scheme.

### 5.3.2 Inverter fabrication and load line analysis

A p-type inverter was fabricated from two devices based on arrays treated by TcEP. Figure 5.8a shows optical micrographs associated with this process. Here, a common source electrode is used to perform TcEP on two arrays with interconnected drain electrodes. Following TcEP, the gate and dielectric layers were removed. For one transistor (the load TFT), the associated source and drain electrodes for TcEP served as electrodes for the final device. For the other (the driver TFT) the source electrode was extended to yield a reduced channel length (~3.5 μm). Finally, new dielectric (SOG/HfO$_2$, 35/20 nm) and topgate (Ti, 70 nm) structures were defined, to complete the fabrication. The current level for the driver TFT increased roughly linearly with the reduction in channel length from 30 μm to 3.5 μm (expected ratio~8.5, measured ratio~9.5). This yielded for a current ratio between driver and load TFTs of ~10.

Figure 5.8b,c shows the electrical properties of the driver and load TFTs. The measured voltage transfer curve (VTC) is consistent with that predicted from load line analysis (Fig. 5.9). Some variation between the measured and predicted VTC curves results from hysteresis in the load and driver TFTs. The measured voltage gain (~4) is near expectation based on conventional diode-load inverter circuit design equation (~3, $A_V=\frac{g_m}{g_{m_{load}}}=\left(L_{load}/L_{driver}\right)^{0.5}$).

### 5.4 Conclusions
In summary, we demonstrated a variety of effective devices based on aligned arrays of SWNT. For the case of RF analog transistors, devices can be created based on unpurified arrays. Here, some increase in performance can be predicted based on purification, however, this is minimal compared to benefits associated with increases in array density. For devices where high on/off is required, TcEP purified arrays offer an excellent means of creating SWNT devices, as demonstrated here.

5.5 Methods

Removing the gate electrode and dielectric. Following TcEP, the purified SWNTs (i.e. consisting only of s-SWNTs) were protected by a patterned layer of photoresist (AZ 5214) prior to removal of the gate metal (for Ti, Transene, Inc; titanium etchant TFTN; for Cr, Transene, Inc; chrome mask ethant-CE-5M 9). Wet etching (H₂SO₄:H₂O₂=2:1, 60 °C, 5 ~10 s) removed the crosslinked PVA. Etching in buffered hydrofluoric acid (BOE 6:1, 30 s) removed the SOG/Al₂O₃ bilayer. Stripping the photoresist completed the process.

Fabricating short channel devices. Following removal of the partial gate transistor structure, phase shift lithography⁴³, electron beam evaporation (2 nm Ti, 25 nm Pd), and lift-off (facilitated by brief ultrasonication, ~30 s) defined a narrow gap separating new source and drain electrodes on a purified array of s-SWNTs. PDMS stamps for phase lift lithography were cast and molded (Dow Corning, Sylgard) from a Si master, fabricated by photolithography (AZ 5214) and Bosch etching (etch/passivation, cycle time: 5s/5s, RIE power: 20 W/0 W, SF₆/C₄F₈ flow: 35 sccm/110 sccm, for constant ICP power of 600 W, etch rate 1 μm/80 s) in SF₆ to a depth of ~1 μm. Following liftoff, the later dimensions of source and drain electrodes were further defined by photolithography (AZ 5214) and a combination of wet and dry chemical etching (Transene Pd
etchant, 50 sec, followed by RIE, CF₄/O₂, 40 sccm/1.2 sccm, 150 W, 30 sec). Dielectric layers of HfOₓ/HfO₂ (47 nm/3 nm) were deposited by ebeam evaporation and atomic layer deposition respectively. Photolithography (AZ 2070), and sputtering (70 nm Ti, 150 W, 3 mTorr Ar, AJA International), followed by lift-off defined gate electrodes, to complete the devices.

**Fabricating inverters.** First, TcEP yielded two purified arrays of s-SWNTs. Photolithography (AZ 5214), electron beam evaporation (2 nm Ti, 48 nm Pd) and lift-off then patterned source and drain electrodes for the driver transistor (L= 3.5 µm, W=30 µm). The electrodes associated with the TcEP processes were used for the load transistor (L=30 µm, W=30 µm). SOG/HfO₂ (35 nm/20 nm) dielectrics were used for both transistors. Photolithography (AZ 5214), electron beam evaporation (100 nm Ti) and lift-off defined the gate electrodes.

### 5.6 References


Leaver, K. D. *Microelectronic devices.* (Imperial College Press, 1998).

5.7 Figures

Figure 5.1 Optical and scanning electron micrographs, cross sectional schematic illustration and representative data from RF SWNT array transistors formed on a quartz substrate. (a) Optical microscope images of a typical device (a) and a collection of devices (inset) (b) showing the RF probe pad configuration and double gate layout. The channel regions of the transistors were fabricated by two electron beam lithography processes; the contact pads with ground-signal-ground coplanar structure were formed by photolithography. The dark region at the center of the device shown in (b) is due to the gate dielectric (50nm thick HfO₂). The channel width ($W$) and length ($L_g$) of this device are 100 µm and 700 nm, respectively. The nanotube density is 5 tubes/µm. (c) Schematic cross sectional illustration of the device layout. (d) Transfer characteristics of the device shown in (b), measured at a drain bias ($V_d$) of -1 V. (e) Output characteristics of this device, for gate voltages ($V_g$) between -1V to 1V, measured in steps of 0.4 V.
Figure 5.2 RF characteristics of an SWNT array transistor whose DC characteristics appear in Figure 1. (a) Amplitude plots of $S$-parameters for frequencies between 0.5 and 50 GHz. (b) Amplitude plots for current gain ($H_{21}$), unilateral power gain ($U$) and maximum available gain (MAG) for frequency between 0.5 and 50 GHz. The unity-current-gain frequency $f_t$ and unity-power gain frequency $f_{max}$ are around 5 and 9 GHz, respectively. (c) Plots of $f_t$ and $f_{max}$ as function of drain bias ($V_d$) at gate bias ($V_g$) of 0 V. (d) Plots of $f_t$ and $f_{max}$ as function of $V_{gs}$ at $V_{ds} = -1$V. (e) Plot of transconductance, as calculated from the slope of transfer curve in figure 1d, as function of $V_g$. The maximum frequencies and the peaks in transconductance appear at approximately the same $V_g$, as expected.
Figure 5.3 Variation of response frequencies \( f_t \) and \( f_{\text{max}} \) with channel length \( L_g \) and channel width \( W \). (a,b) Plot of \( f_t \) and \( f_{\text{max}} \) evaluated at \( V_d = -2.5 \) V and \( V_g = 0 \) V as a function of \( L_g \) for devices with \( W=100 \) \( \mu \)m. (c) Plot of \( f_t \) at \( V_d = -2.5 \) V and \( V_g = 0 \) V as a function of \( W \) for \( L_g=700 \) nm. All devices here in this frame have a nanotube density of 2 SWNTs/\( \mu \)m. (d) Correlation between \( f_t \) and \( g_m \) obtained from data shown in Figure 2d and 2e.
Figure 5.4 Measured and modeled RF response of a SWNT array transistor in a 50Ω system with channel width ($W$) of 100 µm and a channel length ($L_g$) of 700 nm, biased at $V_g = 0$ and $V_d = -1$ V. The device here has a nanotube density of 5 SWNTs/µm. (a) Circuit schematic of the model, with key variables identified. (b) Smith chart of measured and simulated $S$-parameters. (c) Gain if the device were impedance matched, MAG. (d) Reverse isolation of SWNT array transistor. Single-pole roll off with decreasing frequency is due to $C_{gd}$. $C_{gd}$ is directly extracted at low frequencies, in this case at 0.2 GHz.
Figure 5.5 Intrinsic performance of SWNT array transistors. (a) Plot of drain current ($I_d$) associated with the semiconducting SWNTs (i.e. $I_{\text{sem}} = I_d - I_{\text{off}}$ where $I_{\text{off}}$, the off state current, is associated with metallic tubes and is extracted from the minimum in current as a function of $V_g$) for a transistor with $L_g=700$ nm at $V_g = 0$ V as a function of drain voltage, $V_d$. The device saturates at a drain bias of $V_d=-0.5$ V. The device here has a nanotube density of 5 tubes/μm. (b) Plot of $C_{gd}$ and $C_{gs}$ as function of drain voltage. (c) Schematic representation of charge distribution on SWNT at linear and saturation regimes of behavior.
Figure 5.6 TcEP enabled device electronics. (a) Schematic illustration of the geometry of a short channel (L~800 nm) transistor that incorporates an array of s-SWNTs formed by TcEP (~10 SWNT following TcEP). (b) Optical micrograph and SEM image (taken prior to dielectric deposition) of the device. (c) Output characteristics for the short channel device for gate bias $V_{GS} = -3, -2, -1, 0, 1$ V, for a range of $V_{DS} = -2$ to 0 V. Transfer characteristics are inset for $V_{DS} = 0.1$ V (black) and -1 V (red). (d, e) Circuit diagram and optical micrograph of an inverter formed with two transistors that use arrays of s-SWNTs formed by TcEP. (f) Voltage transfer characteristics of the inverter.
Figure 5.7 Details of TcEP in a parallel operational mode. (a) Optical images for a 1 X 5 array of SWNT arrays and associated electrodes for TcEP, with electrodes connected in parallel (b) transfer characteristics before and after TcEP in parallel and (c) transfer characteristics for disconnected individual arrays following TcEP. All arrays show high on/off ratio following TcEP.
Figure 5.8 Details of inverter fabrication  (a) Optical micrographs of process flow for inverter fabrication. TcEP was performed on two arrays in parallel, the gate electrode and dielectric layers were removed, and then new, top-gated TFTs were fabricated with appropriate channel lengths for optimal inverter performance. (b) I-V characteristics of driver FETs associated with electrodes used for TcEP (30 μm channel length) and final device configuration (3.5 μm channel length), respectively. (c) I-V characteristics of driver and load TFTs following inverter fabrication.
Figure 5.9 Inverter fabricated using arrays processed by TeEP. (a) load line analysis for the inverter and (b) voltage transfer characteristics measured and predicted from load line analysis.
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Table 5.1. Values for device parameters calculated from RF modeling.

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<td>4.38E+03</td>
<td>9.7</td>
</tr>
<tr>
<td>AVG</td>
<td>6.80E-06</td>
<td>1.11E-06</td>
<td>9.18E+03</td>
<td>18.3</td>
</tr>
</tbody>
</table>

Table 5.2. Summary of conductance of 1x5 arrays of devices before and after TcEP.
CHAPTER 6

CONCLUSIONS AND OUTLOOK

6.1 Conclusions and outlook

As described in the introduction material, we view the best route to high performance aligned arrays of s-SWNT as one which utilizes CVD of SWNT on single crystal quartz substrates, followed by post-growth treatment to selectively remove m-SWNT. In this work, we studied fundamental aspects of this alignment process and developed a post-growth treatment, TcEP, which allows for highly selective and scalable purification of these arrays. The device demonstrations in chapter 5 represent the realization of this type of approach. We believe that the scalable nature of this approach should create a route for circuit scale demonstrations in the future.

Despite this, the final results achieved using TcEP treated aligned arrays have two notable short-comings. The first is the complex and cumbersome nature of the device electrode architectures that must be fabricated to carry out TcEP and then removed to make room for fabrication of circuits or high performance devices. The second is the SWNT density in the arrays used for these demonstrations (~1-3 SWNT/μm), which is significantly lower than densities required for performances competitive with other materials (~200 SWNT/μm)\(^1\). Fortunately, the studies described here provide insights into directions for future research related to these challenges.

The electrode geometries associated with TcEP are not ideal, however, the basic principle of TcEP centers around the use of induced heating in SWNT to pattern thin organic layers and the scaling and physics associated with this process. Regardless of how heating is
induced, this basic scheme provides the practical benefit of reducing the power for removal significantly and providing complete physical removal. To date, other approaches that utilize heating by means such as electromagnetic radiation have been largely unsuccessful\(^2\), despite well-established differences in optical absorption for m-SWNT and s-SWNT. It is likely that application of TcEP based on optical (or other electromagnetic radiation) exposure would be more effective, based on the dramatic reduction in required power. This type of approach would rely on the underlying principles of TcEP while removing the complex fabrication associated with joule induced TcEP.

Dense purified arrays of SWNT represent a significant challenge. There are two reasonable approaches to achieve them. The first involves the growth and purification of aligned arrays at low density followed by multistep transfer printing to increase the density of arrays\(^3\)\(^-\)\(^5\). Such approaches have been demonstrated on unpurified arrays, but thus far have not achieved necessary densities. Further improvement on these basic techniques, coupled with starting materials consisting of low density TcEP patterned arrays could provide a route to this. The second approach involves fundamental improvement of the growth density of SWNT coupled with improvements to the TcEP process. An important outcome of the study presented in chapter 2 is that growth density is not limited by the mechanism for alignment, but rather the complex dynamics of SWNT growing from dense regions of catalyst particles. Approaches that provide further control of this aspect of the growth could provide advancements in growth density. Alternatively, multiple growths provide a route to this\(^6\). In either case, these improvements should be coupled with improvements to TcEP allowing purification on high density arrays. The studies here utilized modest densities where the process was effective, however at high densities, the width of trenches could provide a fundamental limit such that
trenches associated with m-SWNT exposed neighboring s-SWNT. As, discussed in chapter 4, trenches were observed to form distinctly as closely as 250 nm apart, suggesting for perfectly spaced arrays (where every third SWNT is metallic) TcEP could perform effectively at densities up to 12 SWNT/μm. However, these limitations could also be overcome with improvements to the Tc-resist material. Analytical models indicate that the trench geometry is critically tied to the temperature coefficient of surface tension in the Tc-resist, $\gamma_1$. Additionally, the width of trenches is directly proportional to the film thickness. Thus finding materials with increased $\gamma_1$ that could act as etch resists for the s-SWNT at reduced thickness represents a clear path to high density TcEP.

Given the significant discrepancy between the desired density and the density presented in these demonstrations it is likely that solutions would involve a combination of these two approaches, using fundamental improvements to aligned growth and TcEP to yield starting materials with higher density and achieving further increases to this density via multiple transfer printing.

Overall, we believe that the research presented here represents a significant step towards the goal of high density perfectly aligned arrays of s-SWNT.

6.2 References


