CARBON NANOTUBE FILMS FOR FLEXIBLE ELECTRONICS

BY

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THESIS

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ABSTRACT

Discovering scalable routes to fabricate large scale electronic devices on flexible substrates has been the goal of the newly emerging field of flexible macroelectronics. Thin film transistors (TFTs) have been fabricated on flexible substrates by using organic small-molecule and polymer-based materials, or thin layers of crystalline inorganic semiconductors. Recently, films of carbon nanotubes have been proposed as electronic materials with superior electrical performance due to exceptional electrical and mechanical properties of single-walled carbon nanotubes (SWCNTs). In this thesis, some aspects of recent research efforts on integrating arrays of carbon nanotubes into macroelectronic devices are described.

Carbon nanotube films have two major uses for flexible macroelectronics. The first approach uses carbon nanotube thin films as active semiconducting materials in the channel of flexible TFTs. Even though, high-performance carbon nanotube thin film transistors have been realized, the electronic non-homogeneity of the as-grown carbon nanotubes in the film limits the device performance for some applications. In this thesis, the application of electrochemical functionalization on carbon nanotube films to improve the electronic homogeneity of the film is described. The effect of the crystal quartz substrates on the growth rate of carbon nanotubes, and whether this can be used to sort out as-grown carbon nanotubes by electronic type is also discussed. Finally, I argue that high density carbon nanotube films can also be used as highly conducting stretchable interconnects on mechanically flexible electronic circuits. The sheet resistance and the nature of the buckling of carbon nanotube films on flexible substrates are discussed.
To my husband...
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CHAPTER 1

SINGLE-WALLED CARBON NANOTUBES

1.1 Introduction to Single-Walled Carbon Nanotubes

Carbon element is the foundation of all organic materials. Carbon atoms have an outstanding ability to make compounds with a variety of atoms even in the forms of long polymeric chains with different physical properties. In nature, carbon can be found in many forms and it makes various compounds. For instance, carbon atoms can form quasi one-dimensional tube structures, which are called carbon nanotubes. Carbon nanotubes have attracted interest of many researchers within the last two decades due to its exceptional electrical and mechanical properties.[1] In this thesis, some aspects of recent research efforts on integrating arrays of carbon nanotubes into macroelectronic devices are described.

Carbon nanotubes have attracted interest due to their high carrier mobilities, current carrying capacities and elastic properties.[1-5] The crystal structure of carbon nanotubes can be simply described as a graphene layer rolled into a tube structure. A graphene layer is a two-dimensional honeycomb lattice of carbon atoms. Figure 1.1 shows the crystal structure of a graphene layer. The inherent electrical properties of a carbon nanotube are determined by the chiral vector, along which the graphene is hypothetically rolled to form the nanotube.[1] As shown in Figure 1.1, this vector can be described in the non-orthogonal basis of the lattice vectors of the graphene. Nanotubes are typically named after the chiral vector. For instance, the nanotube is said to be a $(n, \nu)$. 

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$m$) nanotube or a nanotube with $(n, m)$ chirality, if the chiral vector is $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$, where $n$ and $m$ are integers satisfying the basic relation $0 \leq m \leq n$. The crystal structures of several nanotubes are shown in Figure 1.2. If $n$ and $m$ are equal, then the nanotube is called to be an armchair nanotube. Figure 1.2 (a) exemplifies the structure of a $(7, 7)$ armchair nanotube. Armchair nanotubes always exhibit metallic character.\[6\] If $m$ equals to zero, then it is a zigzag nanotube. $(10, 0)$ and $(9, 0)$ zigzag nanotubes are shown in Figure 1.1 (b) and (c). The electrical characteristics of zigzag nanotubes are diverse as seen in Figure 1.3. This figure compares the electrical density of states of $(9, 0)$ and $(10, 0)$ nanotubes.\[7\] The $(9, 0)$ nanotube has finite density of states around the Fermi level, and therefore shows metallic behavior. The $(10, 0)$ nanotube, on the other hand, has an energy bandgap around the Fermi level, therefore it is a semiconductor. All other nanotubes are classified as chiral nanotubes, and they also have diverse electrical properties.

The electrical properties of carbon nanotubes can be determined by the chirality. If the difference between $n$ and $m$ is a factor of three, then the nanotube is assumed to be metallic and have a constant density of states near the Fermi level.\[1\] If that’s not the case then the nanotube is semiconducting and has an energy bandgap, which is inversely proportional to the diameter of the nanotube. In real world, metallic nanotubes, with the exception of armchair nanotubes, also have small bandgaps due to curvature related effects.\[6\]
1.2 Chemical Vapor Deposition Growth of SWCNTs

Carbon nanotubes can be synthesized in the forms of a single shell or multiple shells, for which each shell is a nanotube itself. Carbon nanotubes in the form of multiple concentric shells are called multi-walled carbon nanotubes (MWCNTs). A MWCNT is depicted in Figure 1.4. With improved synthesis methods, on the other hand, carbon nanotubes with a single layer can also be synthesized.[8] These are called single-walled carbon nanotubes (SWCNTs).

The experiments that will be discussed in this thesis have been done on SWCNTs, which have been grown by chemical vapor deposition (CVD). A schematic diagram of our CVD setup is shown in Figure 1.5. SWCNTs are grown from metal catalyst particles by a carbon feedstock gas in the presence of H₂ at high temperatures (840-925 °C). In our experiments, ethanol (EtOH) vapor is the carbon source. EtOH vapor is carried into the CVD system by Ar gas, which is bubbled through liquid EtOH at 0.5 °C.

Figure 1.6 shows scanning electron microscope (SEM) images of SWCNTs grown with different orientations. Figures 1.6 (a) and (b) show aligned SWCNTs grown on single crystal quartz. On the other hands, SWCNTs grow in random directions on Si substrates with oxide layers on top as seen in Figures 1.6 (c) and (d). With current SWCNT growth methods, the chirality of synthesized SWCNTs cannot be controlled. Therefore, SWCNTs with both metallic and semiconducting characters are grown simultaneously.[8] This is one of the greatest challenges to integrate SWCNTs into electronic devices in a scalable fashion.
1.3 SWCNTs Thin Film Transistors

SWCNTs have been proposed as high performance electronic materials for various electronics applications due to their diverse, but yet exceptional, electronic properties.[9] Field effect transistors (FETs), which use semiconducting SWCNTs as the active channel material, have been fabricated already.[10-12] High carrier mobilities of SWCNTs make them desirable for electronics.[13] SWCNT FETs have device mobility values as high as 100,000 cm²/Vs at room temperature.[2] Prototypical logic circuits, chemical sensors, biological sensors, light emitting devices and ring oscillators based on SWCNT FETs have also been fabricated.[14-21] Terahertz operation of SWCNTs has also been shown to be possible due to low capacitance of SWCNTs.[22] However, diverse electronic properties of as-synthesized SWCNTs are hindering the scalable fabrication of SWCNT FETs with consistent device performances. An approach to overcome this problem is to use thin films (sub-monolayer to a few layers) of SWCNTs.[23-26] SWCNT thin films can be produced in wafer-scale.[25] In SWCNT thin film transistors (TFTs), device-to-device performances are more consistent due to statistical averaging and channel currents are high due to large area of coverage in the channel.[25] TFTs with aligned arrays of long (~100 μm) SWCNTs exhibit electrical characteristics that are similar to the devices with individual SWCNTs in terms of device mobility and channel length scaling.[27] Thin films of aligned SWCNTs have been proposed for high frequency device applications.[28,29] TFTs with random networks of SWCNTs, on the other hand, have applications in the emerging field of macroelectronics.[25]
Figure 1.7 illustrates a SWCNT TFT on a doped Si substrate. SWCNT film is contacted by the source and drain electrodes. These electrodes are used to apply the channel bias. For the devices presented in this thesis, electrodes have been patterned by optical lithography, and deposited by electron beam evaporation of bulk gold with a thin titanium adhesion layer. Neighboring devices are isolated by selective reactive ion etching of SWCNT film on the wafer by oxygen plasma. The SWCNTs are isolated from the gate electrode by an oxide layer. The SWCNT thin film is gated through the oxide layer to turn on and off the TFT channel current. SWCNT film can also be gated through another dielectric layer, which can be deposited on top of the film, or by an electrolyte solution.[27,30-32]

The device performance of TFTs, which uses aligned arrays of SWCNTs, is limited by the contribution of metallic SWCNTs.[26,27] This is also true for TFTs of SWCNT networks, either in the short channel limit or if the metallic SWCNTs form a percolating network.[31] In this thesis, some approaches to eliminate the contribution of metallic SWCNTs to the channel current will be described.

1.4 **SWCNT Interconnects**

Metallic SWCNTs have been proposed as interconnects in electronic circuits due to their low resistivities and high current carrying capacities, which can be as high as 1 GA/cm$^2$.[3,33] Recently, carbon nanotube based highly conducting elastic composites have been studied as interconnects in flexible macroelectronic devices.[34,35] On the other hand, very high density films of SWCNTs are good conducting materials with high Young modulus.[36] SWCNTs can be grown in the form of macroscopic films.[37]
Figure 1.8 shows an optical image of O₂ plasma etched lines of SWCNT macrofilms. In the last part of this chapter, electrical conductance of SWCNT macrofilms is studied on flexible substrates as a function of strain.

1.5 Outline of this Thesis

In Chapter 2, post-fabrication chemical functionalization of metallic SWCNTs in the channel of TFTs is discussed. Chapter 3, on the other hand, discusses the dislocation theory of chirality-controlled SWCNT growth on single crystal quartz substrates with an experimental approach. Finally, in Chapter 4, strain dependence of conductivity of SWCNT macrofilms on flexible substrates is described.

1.6 References


Figure 1.1: The structure of two dimensional graphene. Lattice vectors of the graphene and the chiral and translational vectors of the corresponding carbon nanotube are shown and labeled.
Figure 1.2: SWCNTs with different chiralities: A) (7,7), B) (10,0), C) (9,0), and D) (9,1).
Figure 1.3: The density of states of carbon nanotubes with different chiralities (solid lines), and two dimensional graphite (dashed lines). A) (10,0) nanotube, B) (9,0) nanotube. The figure is taken from ref. [7].
Figure 1.4: A multi-walled carbon nanotube.
Figure 1.5: Schematics for chemical vapor deposition of carbon nanotubes.
Figure 1.6: (A-B) Aligned SWCNTs grown on single crystal quartz substrate from Fe catalyst lines. (C) A dense film of SWCNTs grown on Si substrate with thermal oxide from tri-metal (Fe-Co-Mo) catalyst. (D) A random network of SWCNTs grown on Si substrate with thermal oxide from Ferritin catalyst. The scale bars are 100 μm, 10 μm, 1 μm, and 10 μm, respectively.
Figure 1.7: Schematics for a back-gated carbon nanotube transistor.
Figure 1.8: Optical microscope image of a SWCNT macrofilm. Line patterns are etched on the film. The scale bar is 50 μm.
CHAPTER 2

CHEMICAL FUNCTIONALIZATION OF CARBON NANOTUBE THIN FILMS

2.1. Motivation

Transistors, which use single-walled carbon nanotube (SWCNT) films as the active semiconducting material in the channel, have been proposed for many macroelectronics applications on both traditional and flexible substrates.[1-13] However, the channel current in SWCNT thin film transistors (TFTs) cannot be completely turned off unless the surface coverage of metallic SWCNTs is small enough not to form a percolating network and the channel length is greater than length of metallic SWCNTs, limiting the ratio of on current to the off current (on/off ratio).[5,8,14] Therefore, the device performances, especially for digital electronics applications, are limited by low on/off ratios in TFTs, which have finite off-current in the channel.

Several approaches to improve the electronic homogeneity of SWCNT films have been reported. The use of Co-Mo catalyst for SWCNT growth has been reported to increase the yield of (7,5) and (6,5) SWCNTs up to 38% of the overall SWCNT distribution.[15] Plasma-enhanced chemical vapor deposition (PECVD) growth has also been reported to improve the yield of semiconducting SWNTs from ~70% to 89%.[16,17] The most recent advancement in electronically selective growth of SWCNTs has shown that the yield of metallic SWCNTs can be controllably increased to a maximum of 91%.[18] However, none of these methods can grow all-semiconducting SWCNT films.
On the other hand, there have been numerous studies to eliminate the metallic SWCNTs after growth. One simple method is the electrical breakdown of metallic SWCNTs at high biases and at gate voltages such that the semiconducting SWCNTs are not conducting.[19] However, this method is limited to devices with small number of SWCNTs in the channel, and it is less selective than expected, leading to elimination of semiconducting SWCNTs as well as the metallic ones. On the other hand, Arnold et al. have successfully sorted SWCNTs by electronic type using density differentiation.[20] Key disadvantages of this method are that it’s not cost-effective for scalable fabrication, the process time is long, and it requires solution processing of SWCNTs, which involves steps like strong acid treatment to remove silica support catalyst and high-power ultrasonication, degrading the electrical properties and reducing the SWCNT lengths.[20,21] As a scalable and solution processing-free method, photochemical conversion of metallic SWCNTs to semiconductors has been proposed.[22] Unfortunately, this method has been shown to be more diameter selective than being electronically selective.[22]

In this chapter, I will discuss electrochemical functionalization of CVD grown-SWCNT films by diazonium groups to reduce the contribution of metallic SWCNTs to the device conductance.[23] Strano et al. have developed an almost selective chemical reaction of diazonium salts with metallic SWCNTs.[23] As illustrated in Figure 2.1, diazonium reagents covalently bond with SWCNTs. This reaction decreases the conductivity of SWCNTs.[23] Metallic SWCNTs are assumed to be more reactive to diazonium functionalization than semiconducting SWCNTs, because the finite density of states near the Fermi level can stabilize charge transfer-complexes that form intermediate
products.[21,23,24] This chemical has been proposed for scalable elimination of metallic nanotubes in SWCNT films.[25,26] The earlier experiments have been carried out on either TFTs with limited number of SWCNTs (i.e. low yield) in the channel, inefficient gating or long-channel lengths. All these factors may mislead the interpretations. In this chapter, we will summarize our experimental results, which have been conducted on non-depleting TFTs with either aligned arrays of SWCNTs, or short-channel SWCNT networks.

2.2. Methods

Electrochemical functionalization of both aligned and random network SWCNT samples has been studied. Ferritin diluted in distilled (DI) water has been used as the catalyst for CVD growth of SWCNT random networks similar to earlier studies.[2] The density of SWCNTs on the surface can be controlled by the concentration of ferritin. Ferritin has been diluted from 20 times upto 500 times for different yields of SWCNTs for this study. Drops of ferritin catalyst are deposited on the surface by surface wetting by a drop of methyl alcohol. The catalyst is calcined in air at 820 °C to remove the organics around the rich iron core. After cooling back to room temperature, the quartz tubing, which holds the substrate, is sealed and heated under 300 sccm H₂ gas upto 900 °C to activated the catalyst and reach the reaction temperature. At 900 °C, 20 sccm H₂ gas and 20 sccm Ar gas are bubbled through the liquid EtOH for the CVD reaction. The temperature of the EtOH is kept constant at ~ 0.5 °C in a water chiller. The CVD reaction takes place for 20 minutes, and the sample is cooled down to room temperature under H₂ and Ar.
The CVD growth of aligned SWCNTs is very similar. For aligned SWCNTs, single crystal quartz substrates, which have been annealed at 900 °C in air for 8 hours, are used. Fe catalyst lines are deposited by electron beam evaporation of ~0.1 nm Fe on line patterns. Photolithography is used to pattern the lines prior to catalyst deposition. Fe catalyst lines do not require a calcinations step. The optimum reaction temperature is 925 °C, and the rest of the procedure is the same.

Source and drain electrodes are patterned by photolithography and electron beam evaporation after SWCNT growth. In this study the electrodes are 32 nm in thickness, with being 2 nm Ti and 30 nm Au. Multiple devices are patterned at once, and neighboring devices are isolated by removing the SWCNTs outside the channel region by O₂ plasma etching in a reactive ion etcher chamber.

After fabrication of source and drain electrodes, SWCNT channel is functionalized by 4-bromobenzene diazonium tetrafluoroborate (4-BBDT, Aldrich 673405), as it is illustrated in Figure 2.2. Different concentrations of 4-BBDT have been reacted with the SWCNT thin film for 10 minutes at each concentration, and the 4-BBDT solution is washed away with DI water. The gate dependence of the TFT channel currents have been measured and compared before and after each chemical functionalization step. The SWCNT networks were measured by back-gating (silicon oxide thickness is 300 nm) and aligned arrays of SWCNTs were measured by polyethylene oxide electrolyte gating, following the reference [5].
2.3. **Results and Discussions**

We have studied TFTs, which do not deplete completely, for chemical functionalization. The finite off-current is solely form metallic conduction. We have observed the decrease in the off-current as we have functionalized the SWCNTs. Figure 2.3 compares the device performances before and after functionalization by the 4-BBDT salt for TFTs, which have networks of SWCNTs in the channel. Since the channel length is only 25 μm, the device does not deplete completely when turned off. After fabrication, we have annealed the devices in vacuum to improve the contacts and remove any microfabrication residues.[27] Annealed devices have been left in air for 1 day prior to electrical measurements in order to let the oxygen adsorption at the contacts be saturated. The two TFTs shown in Figure 2.3 have the same device geometry, but the number density of the SWCNTs in the channel is different, as it is obvious from the difference in the channel currents. We have applied the 4-BBDT solution the same way for the two TFTs in question. We consider the number of SWCNTs that get functionalized is proportional to the concentration of the salt and the time duration it is applied. In Figure 2.3, the effect of concentration is evident. First, 20 μM 4-BBDT, and then 50 μM 4-BBDT have been applied on the SWCNT film. With functionalization, channel currents have decreased. More concentrated solution decreased the on and off currents even to lower values. One common feature we observe in both devices is that the decrease in the on current is greater than the decrease in the off current. Even though, small gate dependence is expected for many metallic SWCNTs, the observed differences between the changes in on conductance and off-conductance cannot be justified by the elimination of metallic SWCNTs. The data in Figure 2.3 makes it obvious that the selection is not
perfect. The degree of electronic selectivity can be described by the on/off ratio. However, for the two devices shown in Figure 2.3, the on/off ratio responds to diazonium functionalization with qualitatively different trends. Within the amount of functionalization, the on/off ratio changes within ~25%, but it increases in Figure 2.3 (A) and decreases in Figure 2.3 (B). This means that for the former device the metallic SWCNTs have reacted more, whereas, for the latter device, semiconducting SWCNTs reacted more. We have observed this inconsistency on multiple sets of devices. Therefore, we cannot conclude that the chemical functionalization has exhibited selectivity to electronic nature of SWCNTs. However, the analysis of SWCNT networks is complicated due to the existence if nanotube-nanotube junctions, and non-Ohmic scaling for SWCNT number densities near the percolation limit.[14] Therefore, we have repeated a very similar experiment on TFTs, which makes use of perfectly aligned arrays of SWCNTs. Figures 2.4 and 2.5 compare the device performances before and after functionalization by the 4-BBDT salt for TFTs with aligned SWCNTs. We have collected multiple sets of data for each concentration of 4-BBDT within the 20 μM to 100 μM range at incremental time steps. For aligned SWCNT TFTs, the on/off ratio stayed constant within experimental error as we functionalized the channel. Furthermore, the overall change in the on current being ~3 times the change in the change in the off-current also supports the on/off ratio data, assuming one-third of the SWCNTs are metallic. This is true for both of the samples shown in Figure 2.5. Therefore, we have concluded that the covalent functionalization of SWCNT films with diazonium salts is not electronically selective, but possibly selective to the diameter distribution as described by the pyramidization angle model.[28-30]
2.4. **Conclusion**

We have observed that diazonium salts chemically functionalize SWCNT films. The salt concentration and the amount of time it is applied are important parameters. Yet, we have not observed any electronic selectivity; therefore I do not consider diazonium functionalization of SWCNTs as a scalable method for elimination of metallic SWCNTs in TFTs.

2.5. **References**


2.6. **Figures**

Figure 2.1: (A) Diazonium reagents extract electrons, thereby evolving N₂ gas and leaving a stable C-C covalent bond with the nanotube surface. (B) The extent of electron transfer is dependent on the density of states in that electron density near Fermi level leads to higher initial activity for metallic and semimetallic nanotubes. (C) The arene-functionalized nanotube may now exist as the delocalized radical cation, which could further receive electrons from neighboring nanotubes or react with fluoride or diazonium salts. The figure and its caption is reproduced from reference [23] with the permission of the publisher. Copyright © 2003, the American Association for the Advancement of Science.
Figure 2.2: Application of 4-BBDT functionalization on the channel of the thin film transistor. A portion of SWCNTs in the channel go through a covalent reaction with the diazonium reagents. The 4-BBDT solution is cleaned away by DI-water.
Figure 2.3: The gate dependence of the channel current for two different thin film transistors with different SWCNT yields in the channel. The device performances after fabrication, after vacuum annealing at 300 °C, after initial functionalization with 20 μM 4-BBDT and after functionalization with 50 μM 4-BBDT are compared. The on/off ratios and on currents are also compared for the same devices. The channel length is 25 μm. The channels are composed of random networks of SWCNTs. The source-drain bias is -500 mV. The devices were measured by back-gating. The dielectric thickness is 300 nm.
Figure 2.4: The gate dependence of the channel current for two different thin film transistors. The SWCNT channel was functionalized with incremental steps at different concentrations. The device performances after fabrication and after each functionalization step are compared. The on/off ratios are also compared for the same devices. The channel length is 25 µm. The channels are composed of aligned arrays of SWCNTs on quartz. The source-drain bias is -100 mV. The devices were measured by PEO-electrolyte gating.
Figure 2.5: The change in the on- and off-currents for the devices shown in Figure 2.4 with chemical functionalization.
CHAPTER 3

CHIRALITY DEPENDENCE OF CARBON NANOTUBE LENGTH AS-GROWN ON SINGLE CRYSTAL QUARTZ

3.1. Motivation

Aligned arrays of single-walled carbon nanotube (SWCNT) films have been proposed as high performance electronic materials for flexible macroelectronics.[1,2] Thin film transistor (TFTs) with aligned arrays of SWCNTs exhibit very high device mobilities similar to the devices with individual due to lack of resistive nanotube-nanotube junctions.[3,4] Recent advances in carbon nanotube high frequency electronics also opens up new device application possibilities for aligned arrays of SWCNT.[5-7] However, the contribution of metallic SWCNTs into the channel current in these TFTs limits applications in digital electronics.[1,6] In the previous chapter, the possibility of post-synthesis elimination of metallic SWCNTs has been discussed. However, I have not been able to suggest a scalable but still a useful method. In this chapter, the possibility of electronically selective growth of aligned SWCNTs will be discussed.

A recent theoretical study suggests that the SWCNT growth rate on quartz can be determined by the chiral vector of the SWCNT by using a screw dislocation theory.[8] In principle, if the growth rates and the chiral vector are directly related, then the chirality of SWCNTs can be determined by the length. This would be a significant advancement for sorting out SWCNTs by electronic properties during growth. In this chapter, the validity of this theory in real systems is experimentally investigated. Our experiments also have
provided information regarding the dependence of the length on the chirality and
diameter for CVD-grown SWCNTs. No experimental studies have been published before
on this issue according to the author’s knowledge.

3.2. Sample Preparation

ST-cut quartz substrates, which have been annealed at 900 °C in air for 8 hours,
were used to grow aligned arrays of SWCNTs.[4] Registration markers were patterned by
photolithography and deposited by electron beam evaporation of 25 nm Ti. Following
marker deposition, catalyst dashed lines (40 μm by 1 μm) were patterned by
photolithography, and ~ 0.1 nm Fe were evaporated as the catalyst. Prior to growth,
samples were annealed in Ar at 900 °C. After cooling back to room temperature, the
quartz tubing, which hold the substrate, was sealed and heated under 325 sccm H₂ gas
upto 925 °C to activate the catalyst and reach the reaction temperature. At 900 °C, 12
sccm H₂ gas and 12 sccm Ar gas are bubbled through the liquid EtOH for 10 minutes.
The temperature of the EtOH is kept constant at ~ 0.5 °C in a water chiller. After the
chemical vapor deposition (CVD) of SWCNTs, the sample is cooled down to room
temperature under H₂ and Ar.

The samples were characterized by atomic force microscopy (AFM), scanning
electron microscopy (SEM), and resonance Raman spectroscopy. Lengths of SWCNTs
were compared with the diameter and the chiral angle. Figure 3.1 and 3.2 shows typical
AFM and SEM images of a sample. Markers, catalyst dashed lines and SWCNTs are
easily distinguishable in these images. In analysis, data from bundled or crossing
SWCNTs were excluded.
3.3. **Raman Spectroscopy and the Radial Breathing Mode**

Raman spectroscopy is based on inelastic light scattering. Raman scattering is observable on SWCNTs if the incident or the scattered photons are in resonance with real electronic transitions.[9] Radial breathing mode (RBM) is the Raman mode for SWCNTs for which all the lattice points oscillate in phase in the radial direction.[10] The chirality of SWCNTs can be predicted from the RBM peak center.[9] Figure 3.3 illustrates the resonance condition for different electronic band transitions and corresponding RBM peak centers.

In Figure 3.4, a typical Raman spectrum is shown. All the peaks are from the quartz substrate except the one (star labeled) centered at 174 cm\(^{-1}\). This peak corresponds to the RBM band of the SWCNT studied. The incident laser is a He-Ne laser with 633 nm wavelength or 1.96 eV of photon energy. Following the resonance conditions summarized in Figure 3.3, the chirality of the SWCNT is predicted to be (13,7). For an \((n,m)\) SWCNT, the length of the chiral vector is the circumferential length. Therefore the diameter can be calculated as \(\frac{\sqrt{3(n^2+m^2+mn)}}{\pi} a_{c-c}\), where \(a_{c-c}\) is the average C-C bond distance.[10] The chiral angle, \(\theta\), is \(\sin^{-1}\left(\frac{\sqrt{3}}{2\sqrt{n^2+m^2+mn}}\right) m\).[8]

3.4. **Carbon Nanotube Length on Quartz**

Figure 3.5 compares lengths and diameters of SWCNTs. The lengths have been measured by SEM and AFM, whereas the diameters have been measured by AFM. Registration markers have been used to match the AFM and SEM images. There is no
direct correlation between length and diameter. The data is scattered. However, on average SWCNTs with diameters over 1.4 nm are longer than the narrower SWCNTs.

The relation between the chiral angle and the SWCNT length has also been investigated. Chiral angles and diameters have been measured by Raman spectroscopy. Therefore, only resonant SWCNTs can be measured, and only isolated SWCNTs have been analyzed due to ~ 1 μm beam size with 100X objective. Figure 3.6 compares lengths, chiral angles and diameters. There is no trend between the chiral angle and the length of SWCNTs grown on quartz. This may be attributed to the imperfect surface structure of the single crystal quartz substrates.[11] In theoretical calculations, the change in the shape of the SWNTs on substrate is not also included in the calculations, which may change the screw dislocation strains. With this in mind, the diameter starts to gain significance, whereas the differences between different chiral angles become less important. Even on a perfect substrate, both chiral angles and diameters should determine the growth rate for SWCNTs grown on single crystal quartz. Therefore, the chiral angle can be directly correlated to the abundance of SWCNTs rather than the length of them. This hypothesis is not in disagreement with the experimental data presented in reference [8].

3.5. Conclusion

No correlation between the chirality and growth rate has been observed. The diameter and the growth rate is not also directly related, however large diameter SWCNTs are longer on average than narrow diameter SWCNTs. Unfortunately, the
length cannot be used to sort out aligned SWCNTs by electronic type, in disagreement with the screw dislocation theory.[8]

3.6. References


3.7. **Figures**

Figure 3.1: SEM images for low density aligned arrays of SWCNTs grown from narrow catalyst islands on a ST-cut quartz surface with Ti registration markers.
Figure 3.2: AFM image for aligned SWCNTs grown from a narrow catalyst island on a ST-cut quartz surface with Ti registration markers (not shown).
Figure 3.3: RBM peak center vs. the electronic band transition. The labels on top are for corresponding optical transitions between van Hove singularities.
Figure 3.4: Raman spectrum collected by 633 nm He-Ne laser and 100X objective. The peak denoted by a star is the RBM peak for the SWCNT. The other peaks are for crystal quartz substrate.
Figure 3.5: Diameter vs. length for aligned SWCNTs. Data were collected by SEM and AFM.
Figure 3.6: Diameter vs. chiral angle for aligned SWCNTs. Diameters are color coded. The chiral angles and diameters were measured by resonance Raman spectroscopy.
CHAPTER 4

CARBON NANOTUBE MACROFILMS FOR FLEXIBLE ELECTRONICS

4.1. Motivation

Arrays of single-walled carbon nanotube (SWCNT) films have been proposed as novel electronic materials for flexible macroelectronics.[1--6] Thin film transistor (TFTs) with aligned arrays of SWCNTs exhibit exceptional device characteristics on flexible substrates. In these devices, SWCNT film has been an effective semiconductor that is stretchable. Another approach to design mechanically flexible electronic circuits is to interconnect rigid components of the circuit by stretchable conductors. Metallic carbon nanotubes have been proposed as interconnects in electronic circuits due to their low resistivities and high current carrying capacities, which can be as high as 1 GA/cm$^2$.[7--10] Recently, carbon nanotube based highly conducting elastic composites have been studied as interconnects in flexible macroelectronic devices.[3,11] On the other hand, very high density films of SWCNTs are good conducting materials with high Young modulus.[12] In this chapter, structure and electrical conductance of SWCNT macrofilms are studied on stretchable substrates as a function of strain.

4.2. CVD Growth of SWCNT Macrofilms

Carbon nanotube macrofilms are grown on silicon substrates with 350 nm of thermal oxide by chemical vapor deposition (CVD).[1] Fe/Co/Mo trimetal catalyst is used for very high density growth of SWCNTs.[13] The catalyst is prepared by mixing iron acetate (2.05 mg 99.995%, Aldrich), cobalt acetate (2.05 mg, 99.995%, Aldrich) and
molybdenum acetate dimer (1 mg 98%, Aldrich) in a (2:2:1) weight ratio in 20 mL ethanol (EtOH). The mixture is sonicated for 45 minutes. In earlier works, silica suspensions were used as catalyst support. However, we have noticed that silica support is not necessary as shown in Figures 4.1 and 4.2. The catalyst is spin-coated on the substrate twice at 3000 rpm for one minute each. Then, the substrate is placed in a 4 foot-long quartz tube, which is placed in the CVD furnace. The quartz tubing is sealed and Ar is flushed through the system. The furnace is heated under 450 sccm H₂ gas upto 840 °C to reduce the catalyst and reach the reaction temperature. 7 sccm H₂ gas and 56 sccm Ar gas are bubbled through anhydrous EtOH for 30 minutes at 840 °C to grow SWCNTs. The temperature of the EtOH is kept constant at ~ 0.5 °C in a water chiller. Following CVD reaction, the sample is cooled down to room temperature under H₂ and Ar.

Figure 4.1 shows a scanning electron microscope (SEM) image of a macrofilm, which is a very dense network of SWCNTs. The surface coverage (density) of metallic SWCNTs in the film is way above the percolation limit. Therefore the film exhibits metallic behavior even though only one-third of the nanotubes are metallic. As evident from the atomic force microscope (AFM) image in Figure 4.2, the film includes many layers of SWCNTs. We have managed to grow SWCNT films with thicknesses changing from 0.01 μm to 3 μm. While thin samples are transparent, thick films can be easily seen by the naked eye. Inset in Figure 4.1 shows a photograph of a thick SWCNT macrofilm grown across a ~ 1 cm² area. The macrofilm is in black color. To characterize the quality of the film, we have used Raman spectroscopy. Figure 4.3 exemplifies typical Raman spectra collected on the sample shown in the inset of Figure 4.1. In the 100-400 cm⁻¹ range, multiple RBM peaks are observed, meaning that nanotubes are typically SWCNTs.
with diameters between ~0.5 nm and ~2.5 nm. G-band Raman peak is centered at 1590 cm\(^{-1}\), and the ratio of the D-band peak (centered at ~ 1320 cm\(^{-1}\)) intensity to the G-band peak intensity is very small for a carbon nanotube film, suggesting that C-C bonds are predominantly \(sp^2\) bonded with no or very little \(sp^3\) formation, i.e. the SWCNT film is almost defect-free and amorphous carbon materials are not formed during growth.\(^{[14]}\) Therefore, we conclude our CVD-grown SWCNT films are of high quality.

Realizing high-quality SWCNT films, the electrical conductivity of these films are investigated. Square-shaped Ti/Pd (2nm/45nm) electrodes have been patterned by photolithography, and deposited by electron beam evaporator on the surface of the SWCNT macrofilms. Two-terminal resistances between metal electrodes with different channel lengths (separation between the two electrodes) have been measured in the small voltage limit. The results are summarized and fit to a line in Figure 4.4. The slope of the fit line gives the sheet resistance, \(R_S \approx \frac{\partial (R \cdot w)}{\partial L}\), for the SWCNT film, where \(R\) is the channel resistance, \(w\) is the channel width and \(L\) is the channel length. Sheet resistance for the transparent sample (~ 10 nm in thickness) studied in Figure 4.4 is 267 \(\Omega/\square\).

4.3. **SWCNT Macrofilms on Stretchable PDMS**

Combining their low sheet resistance and high Young modulus, carbon nanotube films have been proposed as electrical interconnects for flexible electronics.\(^{[1,12,15]}\) In this section, the structural and electrical properties of macrofilms are investigated under strain on flexible polydimethylsiloxane (PDMS; Sylgard 184, Dow Corning) substrates.

SWCNT macrofilms grown on Si substrates with oxide layer on top are transferred on to PDMS substrates with sacrificial layers of gold and partially cured
poly(vinyl alcohol) (PVA). [5] Figure 4.5 illustrates the transfer process. In summary, SWCNT films are covered by a gold layer (~100 nm thick). 10 wt% PVA in water is solution casted on the gold layer and partially cured at 70 °C. The SWCNT/Au/PVA film is peeled off the Si substrate by an intermediate PDMS stamp and placed on the final PDMS substrate as described in earlier studies.[5,16] After PVA is dissolved in DI water and gold is chemically etched, the transfer process is complete.

Molecular scale buckling of SWCNTs, and one-dimensional and two-dimensional semiconducting crystals has been studied earlier by transferring these materials on pre-strained PDMS substrates.[16--19] We have used a similar approach to study the SWCNT films. Figure 4.6 exhibits the buckling of a two-dimensional SWCNT macrofilm on an elastomeric substrate (PDMS for our experiment) that has been strained before the transfer process (pre-strained) in one direction. The critical strain necessary to buckle a SWCNT film on PDMS can be estimated as

$$0.52 \cdot \left[ \frac{E_{pdms} (1-\nu_{swnt})^2}{E_{swnt} (1-\nu_{pdms})^2} \right]^{2/3},$$

where the E is Young’s modulus, ν is Poisson’s ratio. Following the literature values ($E_{pdms} = 2$MPa, $\nu_{pdms} = 0.48$, $E_{swnt} = 4.5$ GPa, $\nu_{swnt} = 0.08$) the critical strain ($\epsilon_c$) is calculated to be 0.4%.[12,18,20] The optical microscope images in Figure 4.6 suggest that the period of buckling increases with the amount of pre-strain as expected.[20] For a buckled film, the theory suggest that the period of buckling is inversely proportional to

$$[(1+\epsilon_{pre})(1+\frac{5}{32}\epsilon_{pre}(1+\epsilon_{pre}))^{1/3},$$

where $\epsilon_{pre}$ is the amount of pre-strain on the elastomeric substrate.[12,21] We have observed the decrease in the buckling period with increasing pre-strain. Yet, the buckling period is not uniform. Figure 4.7 shows an AFM
image of a buckled SWCNT film. The AFM image suggests that the non-homogeneities on the surface may be responsible for the non-uniform buckling of the film.

4.4. Conclusion

We have managed to grow SWCNT films in macroscopic sizes with varying thicknesses. The sheet resistances of SWCNT films have been measured and found to be low enough for application in macroelectronics. We have transferred SWCNT films on pre-strained elastomeric substrates and studied the nature of the buckling.

4.5. References


4.6. Figures

![Large area SEM image of a SWCNT film. (Inset) Picture of a thick SWCNT film in macroscopic sizes (~ 1 cm²) as-grown on a Si/SiO₂ substrate.](image)

Figure 4.1 Large area SEM image of a SWCNT film. (Inset) Picture of a thick SWCNT film in macroscopic sizes (~ 1 cm²) as-grown on a Si/SiO₂ substrate.
Figure 4.2 AFM image of a SWCNT film.
Figure 4.3 Representative Raman spectra on the sample shown in the inset of Figure 4.1 by a 10X objective and a 633 nm laser.
Figure 4.4 Width normalized resistance $R^w$ measured between two metal electrodes as a function of the separation between the electrodes ($L$) for a thin high density SWCNT film. The slope, i.e. the sheet resistance, is measured as 267 $\Omega/\square$. 
Figure 4.5 Optical microscope images of high density SWCNT films transferred on a pre-strained PDMS substrate with A) 0%, B) 2%, and C) 5% strain. The SWCNT films have been patterned into lines of 50 μm width by photolithography and RIE etching prior to transferring.
Figure 4.6 AFM image of a high density SWCNT film after getting transferred on a 5% strained PDMS. The strain was applied in the y-direction. The buckling is not uniform, possibly due to surface roughness of the as-grown film and chunks of catalyst particles.
CVD growth of SWCNT film → Au/PVA film deposition → PDMS

Pre-strained PDMS → Stamping

Figure 4.7 A schematic description of the transfer process.
CHAPTER 5

CONCLUSIONS

Carbon nanotubes have been proposed as high-performance electronic materials due their high mobility, current carrying capacity and Young modulus values. In this thesis, several aspects of recent research efforts on integrating arrays of carbon nanotubes into macroelectronic devices have been described.

Due to the structure dependent diverse electronic properties of single-walled carbon nanotubes (SWCNTs) exhibit both metallic and semiconducting characteristics. Ultra-thin films of SWCNTs can be used as effective semiconductors in transistor channels. Especially, if the film is composed of aligned arrays of SWCNTs, then the device mobilities are very high. Unfortunately, metallic SWCNTs in these films can contribute to the channel current, degrading the transistor performance. In this thesis, I have studied two methods, which had been proposed to enhance the electronic homogeneity of SWCNT films by earlier studies. In chapter 2, I have discussed the covalent chemical functionalization of SWCNT films by diazonium salts. In our experiments, we have observed that many SWCNTs in the film are functionalized by the diazonium reagents without any electronic selectivity. Our results suggest that this chemical functionalization method, which had shown limited success in eliminating metallic SWCNTs in transistors with small numbers of SWCNTs, may not be scalable to films with large numbers of SWCNTs. In chapter 3, I have argued whether the interaction between aligned SWCNTs and the underlying crystal quartz substrates may be used to sort out SWCNTs by electronic type. Earlier theoretical studies have shown that the
growth rate of SWCNTs on crystal substrates is affected by the chirality of those SWCNTs. However, any correlation between the SWNT chirality and the growth rate has not been observed in our experiments on vendor supplied quartz substrates, which do not have perfectly smooth surfaces.

Finally, I have argued that high density carbon nanotube films can also be used as highly conducting stretchable interconnects for flexible macroelectronics. We have managed to grow SWCNT films in macroscopic sizes with varying thicknesses. We have measured low sheet resistances for SWCNT films. The nature of the buckling of carbon nanotube films on flexible substrates has also been studied. SWCNT films transferred on pre-strained elastomeric substrates have been shown to buckle. A decrease in the buckling period has been observed with increasing pre-strain. However, the buckling patterns on SWCNT films are not uniform due to varying film thickness along samples and the catalyst particles in the film.
AUTHOR’S BIOGRAPHY

Zulal Tezcan Ozel was born in Eregli, Turkey on July 16th 1983. She has received her B.S. degree in physics from Bilkent University in 2007. She got married in the same year. She began her graduate study in the Department of Materials Science and Engineering at the University of Illinois at Urbana-Champaign in 2008. During graduate school, she was sponsored by the Turkish Ministry of Education (2008-2009).

Her current research interests include solid state device physics, nanotechnology and electronic materials. Following graduation, she will assume a visiting research position in the National Institutes of Health in Bethesda, MD.