Carbon Nanotube Applications for CMOS Back-End Processing

by

Tan Mau Wu

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Abstract

Carbon nanotubes are a recently discovered material with excellent mechanical, thermal, and electronic properties. In particular, they are potential ballistic transporters and are theorized to have thermal conductivities greater than any other material currently known.

In this thesis, we will examine two possible applications of carbon nanotubes in CMOS back-end processing. The first application is as a replacement for copper interconnects. As interconnect linewidths shrink, the electrical resistivity of copper will rise dramatically due to surface scattering effects. Carbon nanotube ballistic transporters may be able to overcome this obstacle, as well as being able to withstand current densities much greater than copper. The second application is a enhanced thermal conductivity dielectric for thermal management purposes. Carbon nanotube-oxide composites demonstrate improved thermal characteristics, and integration into CMOS technology may be able to alleviate some of the heat-removal and distribution problems future integrated circuits will face.

We will also examine some of the processing techniques that will be necessary for carbon nanotube commercial deployment. Some of the issues we will discuss are nanotube growth, purification, and separation. In addition, we will consider some of the specific issues that need to be addressed for carbon nanotube integration into CMOS back-end technology, such as *in situ* growth and self-assembly.

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Acknowledgments

When I first embarked upon the research path leading to this thesis, I did not realize that so much of it would be interdisciplinary. Developing a carbon nanotube interconnect for CMOS *sounds* like it should be an electronics engineering endeavor, but the preparation and supporting framework is also composed of chemistry and materials science. I would like to thank my advising professors Rafael Reif and Francesco Stellacci for recognizing this long before I did and guiding me to the right path. I would also like to thank my colleagues in both of my research groups for their advice and companionship. My parents of course deserve my greatest thanks - what I am is because of them.

Before this starts sounding too misty-eyed, I want to point out that my work here is not done; this thesis is just the beginning of what I'm hoping to accomplish in the doctoral program. That's at least another three years . . . Here's to the future.

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Chapter 1

Introduction

1.1 Motivation for this work

The motivation of this thesis is to examine some of the possible applications that carbon nanotubes have in CMOS technology. Many researchers are focused on developing carbon nanotube-based active devices to replace current MOSFET technology. We are not interested in a wholesale replacement of CMOS technology with nanotube-based processes; rather, we are trying to identify areas of weakness in current back-end technology that carbon nanotubes can help bolster. In particular, we hope to take advantage of carbon nanotubes' excellent thermal and electronic properties in the CMOS back-end to alleviate interconnect and thermal problems.

1.2 Introduction to carbon nanotubes

Carbon nanotubes, discovered in 1991 by Sumio Iijima of NEC, are a promising new material with a host of useful properties. They are able to withstand high currents, are 1-D conductors and theoretical ballistic transporters, and are potentially one of the best thermal conductors known. In addition, they possess good mechanical properties.

1.2.1 Carbon nanotube structure

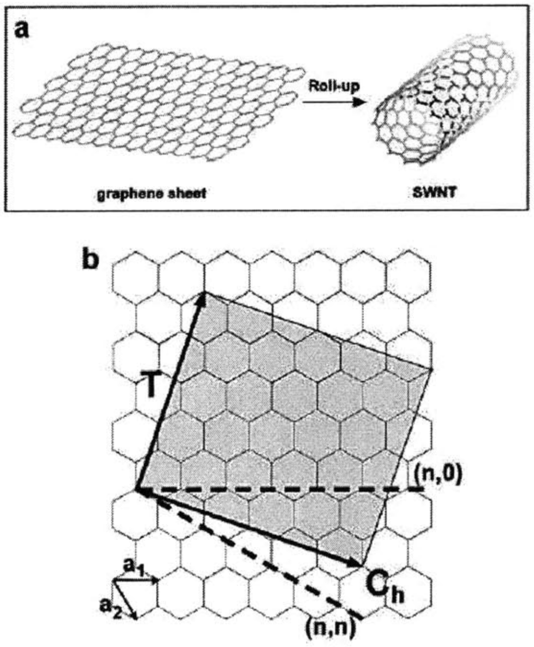


Figure 1-1: Structure of a single-walled carbon nanotube. The chirality of a nanotube is defined by the roll-up vector $C_h = m * a_1 + n * a_2$ or (n,m). The vector T points in the nanotube axial direction.[1]

Carbon nanotubes (CNTs) are fullerene-like structures composed of carbon atoms linked to each other with sp^2 bonds. The simplest kind of carbon nanotube is a single-walled nanotube (SWNT). It can be visualized as a single sheet of graphite (graphene) that has been rolled up into a tube, as seen in Figure 1-1.

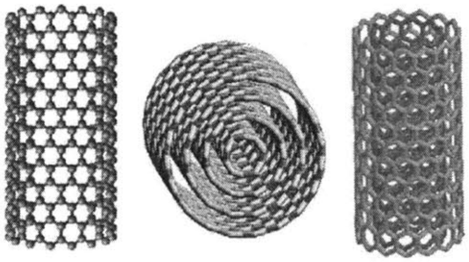


Figure 1-2: Possible multiwalled carbon nanotube morphologies.

Figure 1-2 depicts a more complicated carbon nanotube, the multi-walled nanotube (MWNT), which is composed of two or more SWNTs within each other, much like an elongated onion. Carbon nanotube shells can be distinguished by the way they are wrapped, known as *chirality*, which is defined by a roll-up vector, $c = m * a_1 + n * a_2$ or (n,m). This vector maps two identical but displaced points on the graphene plane, and the nanotube associated with this vector is formed by rolling the plane along the vector such that the two identical points are superimposed on each other (see Figure 1-1. The chirality of a nanotube determines many of its properties, such as diameter and bandgap. In addition, carbon nanotubes can form junctions of different diameters, as well as fork from one nanotube into two nanotubes. As-grown CNTs can vary greatly in diameter and length. SWNTs generally have diameters ranging from 0.4 nanometers (nm) up to about 3 nm, whereas MWNTs, since they are composed of multiple SWNTs, range from 3 nm up. CNT lengths can vary from hundreds of nanometers up to microns, depending on growth conditions. CNTs of up to millimeters in length have been grown, but are fairly difficult to obtain.

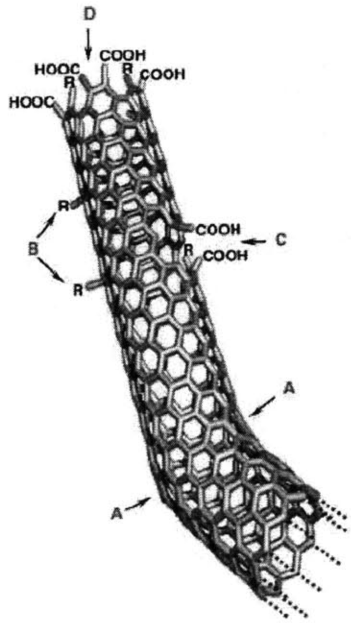


Figure 1-3: Defects in a carbon nanotube can consist of A) 5 or 7-membered rings, B) sp^3 defects, C) sidewall holes, or D) end holes.[2]

Generally, CNTs are depicted as pristine tubes of neatly-arranged carbon atoms. In reality, nanotubes can suffer from a number of defects (see Figure 1-3). The Y-junctions described above result from pentagonal or heptagonal carbon rings in the nanotube structure, as opposed to the normal hexagonal ring shape. These five- and seven-member structures can also cause nanotubes to bend, and are more susceptible to damage because of their strained structure. Nanotube ends are capped with structures formed of these strained rings, and so are more likely to be damaged than the sidewalls. In addition, sp^3-type defects may also be present, where a hydrogen or oxide group is bound to a carbon atom. Finally, under oxidative condition, the carbon structure may be damaged, creating a hole lined with carboxy groups such as carboxylic acids and ketones.

1.2.2 Carbon nanotube electronic properties

The electronic structure of a carbon nanotube is similar to the two-dimensional structure of graphene. However, since a CNT is essentially a graphene sheet wrapped into a tube, quantizing electron momentum along the circumference, its electronic structure becomes one-dimensional. The boundary conditions associated with this quantization also determine the metallic or semiconducting nature of the nanotube. Graphite itself is mostly semiconducting, but has zero bandgap at certain points in k-space. If a graphene sheet is folded to form a nanotube, and the 1D subbands resulting pass through one of these zero-bandgap points, then the CNT will be metallic. If the subbands do not pass through one of these points, then the nanotube will be semiconducting. In addition, the diameter of the nanotube is inversely related to the separation of the allowed 1D subbands. Larger diameter semiconducting CNTs will have smaller bandgaps, and vice-versa. Finally, the curvature of a CNT will create small bandgaps in some metallic nanotubes due to mixing of bonding and antibonding orbitals. The 1D nature of CNTs means that they are ballistic transporters, with a minimum theoretical resistivity calculated via Landauer theory of 6.45 kohms. There are several other factors that can influence this resistivity, such as contact quality and short-range scatterers (more extensive needed).

1.2.3 Carbon nanotube thermal properties

Carbon nanotubes could potentially be one of the best thermal conductors available. Other carbon materials, such as graphite and diamond, have exhibited the highest known thermal conductivities, in the thousands of W/m K. Theoretical calculations indicate that the room-temperature thermal conductivity of a carbon nanotube can be as high as 6600 W/m K[14]. In addition, it has been shown that the thermal conductivity of carbon nanotubes is phonon-mediated at all temperatures, meaning that electrons do not contribute any sort of thermal conductivity[15].

1.3 Summary

In this chapter, we discussed the structure of carbon nanotubes and some of their interesting electronic and thermal properties. In the next chapter, we will examine some of the challenges facing CMOS back-end technology today, specifically in the arena of interconnect design, and consider how carbon nanotubes could be utilized to overcome these obstacles.

Chapter 2

Carbon Nanotubes for CMOS Interconnects

Carbon nanotubes have excellent mechanical, electronic, and thermal properties. The first and most obvious application in terms of electronics engineering is the use of CNTs for device interconnects. We believe that the unique characteristics of carbon nanotubes can address some of the biggest problems in current CMOS interconnect technology, and that CNTs could be a viable replacement for copper interconnects.

2.1 The interconnect scaling problem

As integrated circuits become more complicated and the active devices on a chip become smaller and more numerous, the interconnections on the chip will also grow in complexity and length. At some point, power losses and delays in a circuit due to interconnects will outstrip losses from devices; in fact, this is already the case, and the situation is likely to grow worse.

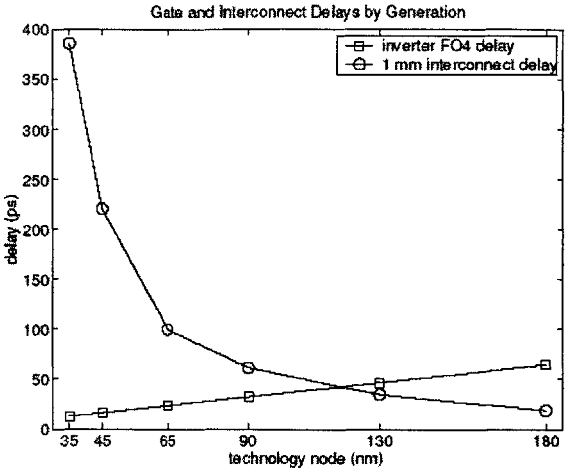


Figure 2-1: Comparison of FO4 inverter delay and the ITRS 1 mm interconnect delay.[3]

Coupled with this increase in complexity is a decrease in wire pitch, which introduces another problem: electrical resistivity. Copper, the state-of-the-art interconnect material, has a bulk electrical resistivity value of 1.7 $\mu\Omega$-cm, and the 2003 International Technology Roadmap for Semiconductors (ITRS) assumes that the effective resistivity for copper/barrier interconnects will remain at 2.2 $\mu\Omega$-cm for the foreseeable future. However, as the diameter of a copper wire approaches the mean free path of electrons in the wire, about 40 nm, its resistivity will increase dramatically due to electron surface scattering effects.

In addition, the ITRS predicts that the maximum current density Jmax required for intermediate wiring will increase to 3.0×10^6 A/cm^2 by the end of this decade and will reach 6.9×10^6 A/cm^2 by 2018, at the 18nm technology node. The maximum current density

Practical Constraint	Global Interconnects Resistance (Ω/mm)	Semi-global Resistance (Ω/mm)	Local Resistance (Ω/mm)
None:ideal $\rho = 1.7\mu\Omega$-cm	628	1773	3275
P=0.5,BT=0	908	2668	5030
P=1,BT=10 nm	1123	3942	8490
P=0.5,BT=10 nm	1192	4351	9564

Table 2.1: Simulated copper interconnect resistance in 2014.[12]

copper can handle is about 10^6 A/cm^2 before electromigration effects make interconnect lifetime unacceptable. Thus, new interconnect strategies will become necessary.

Year of Production	2010	2012	2013	2015	2016
Jmax (A/cm^2)	3.0E06	3.7E06	4.3E06	5.1E06	5.8E06
Conductor effective resistivity ($\mu\Omega$-cm)	2.2	2.2	2.2	2.2	2.2

Table 2.2: Long-term ITRS-projected current densities and conductor effective resistivities.[13]

Carbon nanotubes, with their extremely low resistivities and high achievable current densities, may be a suitable alternative material to replace copper. Their potential ballistic transport properties could lead to an interconnect structure where length is independent of conductivity. Since ballistic transporters dissipate heat at their terminals rather than throughout their length, they could facilitate novel heat removal solutions.

Figure 2-2 compares the resistance of a 1 μm deep via made of various types of material as a function of via width. Ideal ballistic transport properties are assumed for the CNTs, and data for aluminum and copper were obtained from (cite). The ideal SWNT via demonstrates the best performance. The MWNT vias are unable to approach the performance of

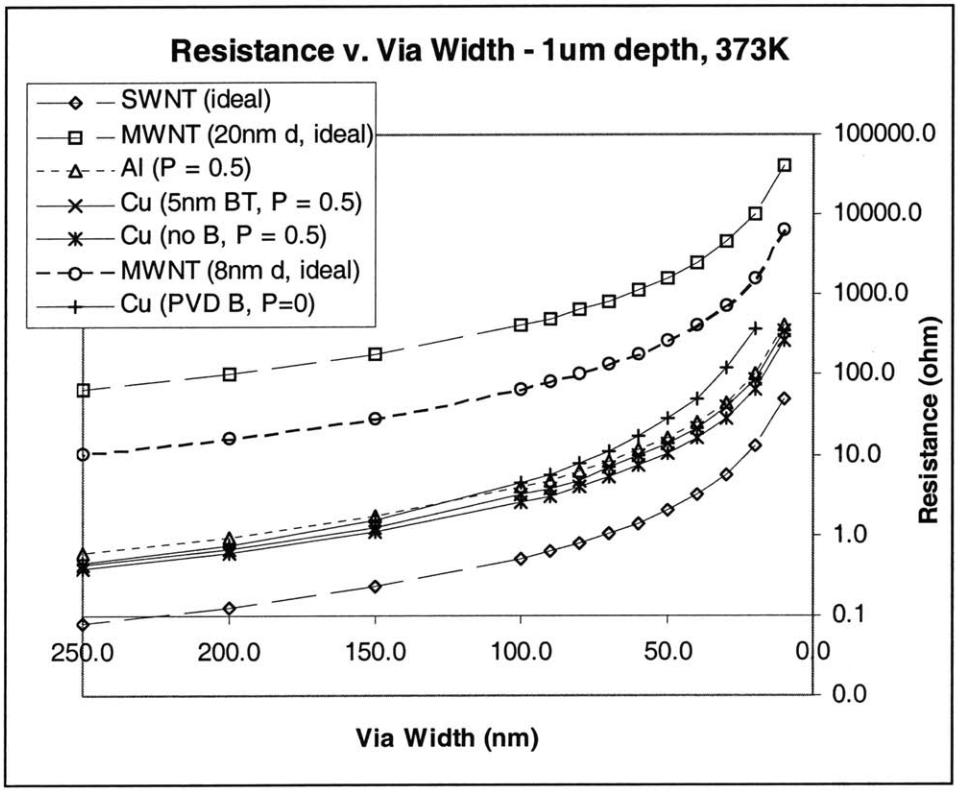


Figure 2-2: Simulated data comparing ideal nanotube vias with aluminum vias and copper vias fabricated with atomic layer deposition (ALD), physical vapor deposition (PVD), and with various barrier thicknesses. P denotes the surface quality of the interconnect, which determines inelastic scattering.

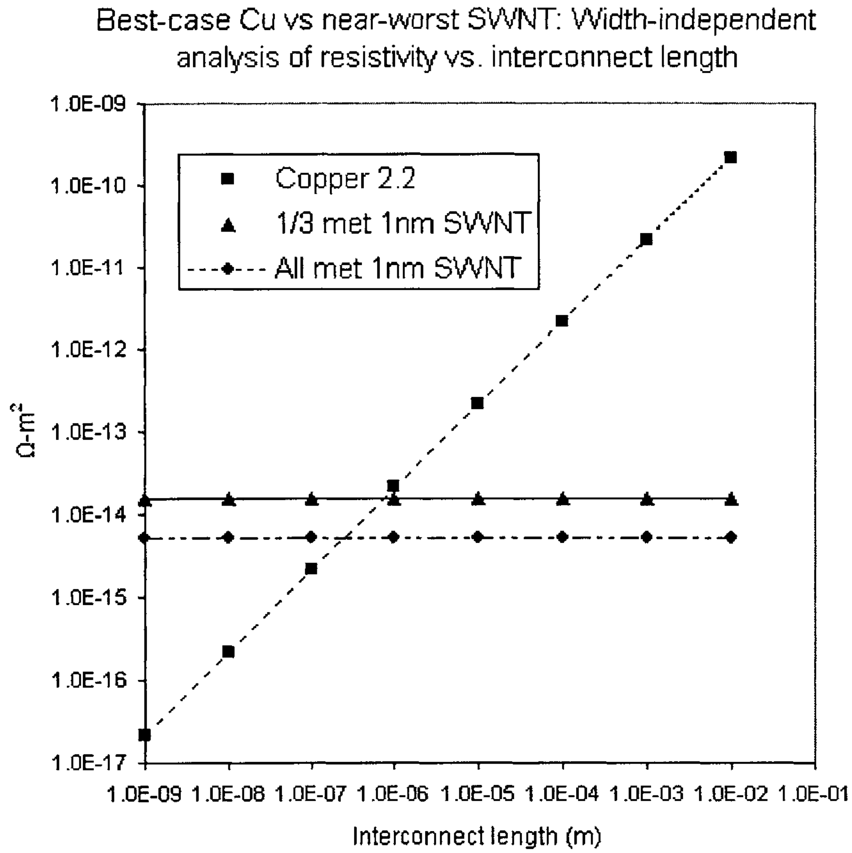


Figure 2-3: A comparison of an ideal bulk copper interconnect with no barrier layer with ideal ballistic SWNT lines, of varying metallic nanotube composition.

even standard metal vias because of size: the parallel MWNT via cannot contain enough of these larger MWNTs to decrease the via resistance to levels competitive with metal vias. However, one advantage that this comparison does not take into account is resistance to electromigration. In this case, the nanotube-based vias have a clear advantage, with maximum current densities more than three orders of magnitude greater than metals.

A best-case copper versus ideal SWNT interconnect comparison is presented in Figure 2-3. Assuming the resistivity of copper remains at the current level of $2.2\mu\Omega$-cm, an ideal CNT interconnect composed of one-third metallic tubes, each 1nm in diameter and with 6.45 kΩ resistance, will have lower resistivity than an equivalently-sized pure copper line at about the 1μm mark. A CNT line of all metallic SWNTs will reach this threshold at about 300nm. Of course, in reality the resistivity of copper will not remain at $2.2\mu\Omega$-cm; in addition, a practical interconnect also has a barrier layer to prevent copper from diffusing into the surrounding oxide. Thus, the *effective conductivity*, defined as the conductivity of the copper material and the associated barrier layer, of the actual interconnect will be much higher. It is true that current nanotube technology is extremely limited - for example, current nanotubes are able to achieve ballistic transport on micron length scales only at extremely low temperatures, and nanotube placement/patterning technology is only in its infancy. However, there is no foreseeable way to push the current copper process for more than a few generations at most. A replacement technology will become necessary, and carbon nanotube-based processes, from a theoretical standpoint, are a promising alternative.

2.2 Summary

In this chapter we discussed some of the problems interconnect technology will face as feature sizes decrease. As the complexity of interconnect structures increase, wiring resistive losses and delays will outstrip losses and delays from active devices. In addition, we are rapidly approaching a linewidth limit imposed by rising resistivity due to the mean free path of electrons in copper and the current capacity of copper lines. We believe that carbon nanotubes, as theoretical ballistic transporters with high achievable current densities, could be a possible substitute for copper as interconnect material.

Chapter 3

General Carbon Nanotube Processing

Carbon nanotubes that are intended for commercial use will generally have to undergo several processing steps. The first and obvious step is nanotube growth in bulk quantities. While some applications may be able to utilize the as-grown nanotube material, for most purposes, the raw CNT material will have to be purified and separated by different parameters.

3.1 Carbon nanotube growth

CNT growth is a high temperature catalytic process. In general, CNT growth occurs when a metallic catalyst serves as a seed into which high-energy carbon atoms dissolve, resulting in an extruded, well-ordered tubular structure.

Several common CNT growth methods are electric arc-discharge, laser ablation, and chemical vapor deposition. In the electric arc-discharge method, a graphite electrode doped with metal catalyst particles is used. When a high voltage is placed across the electrodes, the

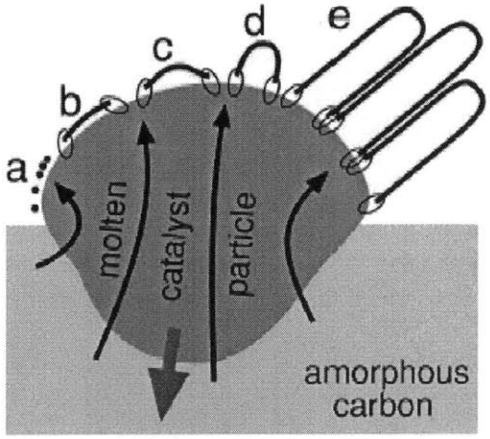


Figure 3-1: A proposed mechanism for CNT growth is via extrusion of carbon atoms from a carbon-saturated molten catalyst particle[4].

resulting arc supplies the energy needed to dissociate the carbon atoms in the graphite, and CNT growth results. With laser ablation, a graphite target, also doped with metal catalyst, is vaporized with a high-energy laser, and the resulting gas deposits on surfaces within the reactor in the form of CNTs.

Chemical vapor deposition (CVD) is similar to laser ablation in that CNT growth results from the coalescence of carbon gases on a surface; however, the gaseous feedstock in CVD is usually a simple hydrocarbon such as methane or carbon monoxide, and the energies needed for CNT formation is supplied by the high temperature in the reactor. Metal catalysts can either be supplied as another gas, or pre-patterned onto a substrate that is placed within the reactor. In general, while all three methods are suitable for supplying CNTs suitable for laboratory research, the CVD processes are more easily scalable for industrial applications.

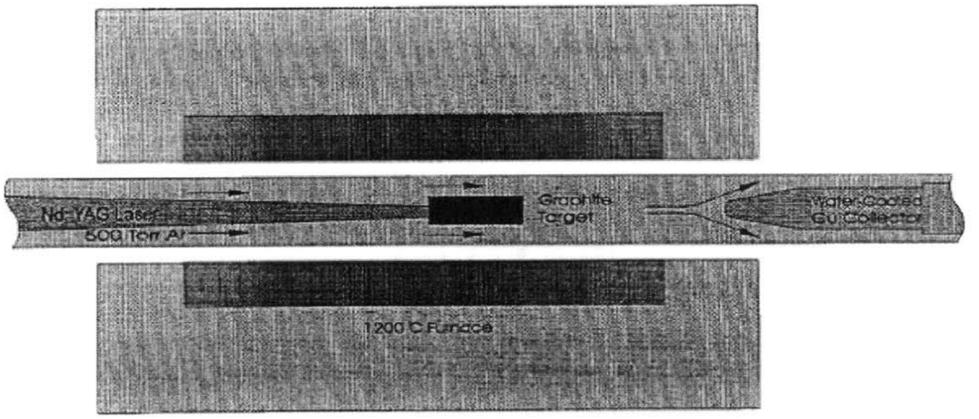


Figure 3-2: A typical reactor for laser ablation CNT growth. The resulting superheated carbon and metal catalyst particles are blown away from the graphite target, with CNT growth occurring in midair, and condense on the cooled collector[5].

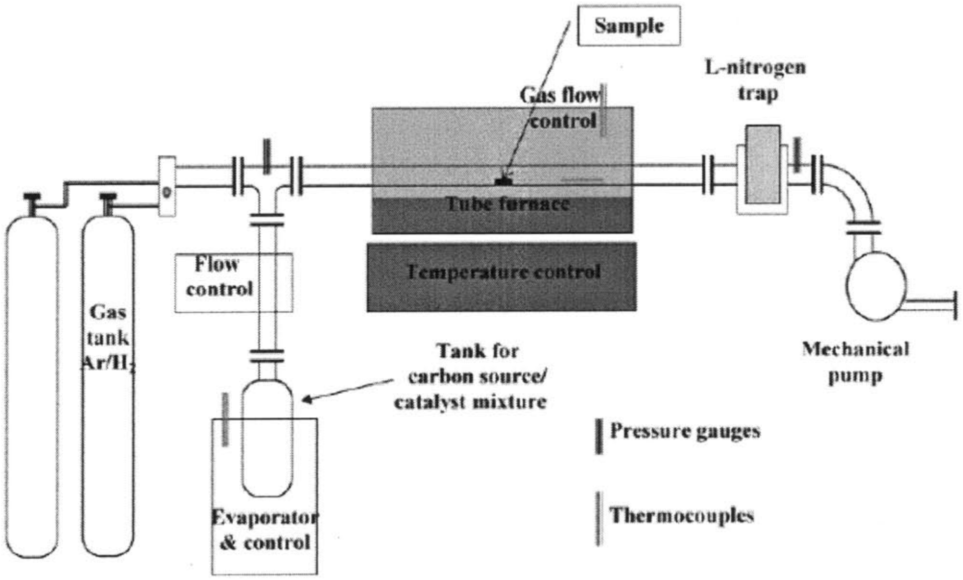


Figure 3-3: A CVD growth reactor. The carbon/catalyst feedstock is streamed into the furnace and deposits on the sample[6].

3.2 Carbon nanotube purification

As-grown nanotube material is generally composed of metal catalyst particles, amorphous and fullerene-like carbon structures, and actual nanotubes. It is desirable to remove as much of the metallic and non-nanotube carbon material as possible before any further processing, both for ease of characterization and to prevent any unwanted side effects in future processing steps. Of course, the actual purification is not a particularly easy task. The as-grown CNT material usually consists of a tangle of nanotube material, with non-nanotube carbon material adhering strongly to both nanotube sidewalls and each other. In addition, the mass is studded with metal catalyst particles coated with a tough shell of amorphous carbon. Coupled to this is the strong Van der Waals attraction between nanotube sidewalls, leading to huge bundles of tightly-bound CNTs with non-nanotube carbon and metal trapped in between. The difficulty of separating CNT bundles into separate CNTs, as well as in breaking through the metal catalysts' carbon shell and in differentiating between the non-nanotube carbon material and actual CNTs make purification a rather dicey endeavor. In order for any nanotube purification scheme to be successful, it has to be able to a) remove metallic catalyst particles and b) destroy amorphous and non-nanotube carbon.

3.2.1 Metal catalyst removal

Of all the impurities that are contained in raw CNT material, the easiest to remove are the metal catalyst particles. Iron and nickel particles are ferromagnetic and can easily be dissolved in acid, and metal purification techniques make use of these characteristics, by

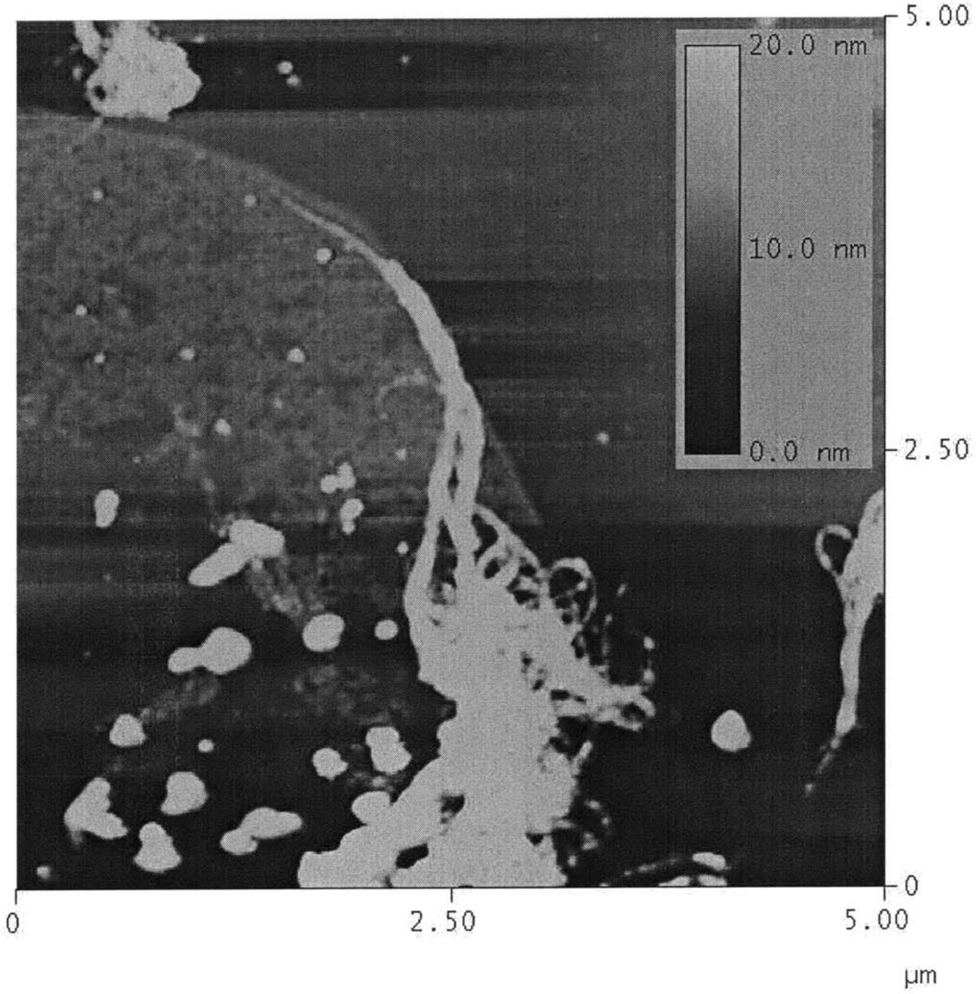


Figure 3-4: A sample of raw HiPCO-grown SWNTs, suspended in dichloromethane (DCM) and deposited on silicon.

either dissolving metal in acid or segregating the catalyst from the carbonaceous material by application of magnetic fields. However, a typical catalyst particle present in raw CNT material is usually covered in a shell of amorphous carbon, which is extremely difficult to remove. Strong nitric or sulfuric acid treatment, also used to oxidize unwanted carbon material, can destroy this amorphous carbon shell, but will also damage nanotube material and introduces several other downstream problems. To circumvent this, a modification to the acid dissolution technique involves treating the raw nanotube material in a low-temperature oven in the presence of water and oxygen. This method oxidatively cracks the carbon shell surrounding the metal particles, and once the metal is exposed, treatment with weaker hydrochloric acid will dissolve the catalyst particles, which can then be filtered out[16]. An alternate method particularly effective with iron particles uses microwaves to selectively heat the metal particles, which also has the effect of oxidizing and cracking the carbon shell[17].

3.2.2 Amorphous/non-nanotube carbon removal

As mentioned above, heating at high temperatures will oxidize non-nanotube carbon, and this has been demonstrated as an effective purification technique for MWNTs, but not so for SWNTs. The metal catalyst particles necessary for SWNT growth seem to facilitate the oxidation of SWNT material at the purification temperatures[16]. If the metal particles are removed before the heat treatment, SWNTs can be purified fairly well with this technique. However, since efficient metal particle removal requires acid treatment, an obvious next step would be to also use an acid treatment to remove the amorphous and non-nanotube carbon.

One of the requirements for effective acid treatment is to disperse or solubilize the CNT material in some sort of liquid. Solubilizing carbon nanotubes is also a key first step to CNT chemistry, which will become important. With the enormous affinity CNTs have for each other, this is no easy matter. Pure nanotube material is not soluble in any solvent; if some amount of raw CNT material is placed into any sort of solvent, it will just sink to the bottom and sit there. A means for dispersing the CNT material is needed, and in general this is done via sonication. A sonicator is a device that uses sound waves in the kilohertz range to create and destroy tiny bubbles in a liquid in a process known as cavitation. The collapse of the bubbles in the cavitation process is an energetic process, both physically and thermally, and this helps break raw nanotube material into smaller pieces and disperses them in the solvent.

The main obstacle to removal of the non-nanotube carbon material in raw CNT material is the difficulty of chemically distinguishing between different carbon forms. Therefore, any chemical method that destroys the non-CNT carbon, such as acid treatment, will also destroy CNTs. Despite this, acid treatment is commonly used for CNT purification. Sulfuric acid, nitric acid, or a mix of varying molarities is added to raw CNT material and heated at reflux temperature for hours up to days. As one might expect, the higher the molarities of the acids used and the longer the purification continues, the more carbon material is destroyed, both non-nanotube and CNT.

A limited study comparing the use of various concentrations of nitric acid for varying reflux times has concluded that refluxing 7 M nitric acid for 6 hours produces the best

sample	YLD%	MET%	SWNT%	CIMP%	metal wt loss (mg)	carbon wt loss (mg)
raw SWNT		41	29	42		
3M HNO_3/12h	69	6.3	34	60	237	73
3M HNO_3/24h	63	4.6	19	76	252	118
3M HNO_3/48h	58	2.9	21	76	264	156
7M HNO_3/6h	65	4.2	30	66	254	96
7M HNO_3/12h	46	3.9	19	77	263	277
16M HNO_3/6h	28	3.4	23	73	272	448
16M HNO_3/12h	14	0.2	2	98	281	579

Table 3.1: Results from the study done by Hu et al on nitric acid purification. Note that CIMP is the percentage carbonaceous impurity in the sample.

yield of CNTs[18]. In addition to oxidizing carbon, treatment with strong acids also does a reasonable job of removing metallic catalyst impurities from the raw material, probably by digesting the carbon shell surrounding the particles and dissolving the exposed metal.

An alternative process that may be conducive to purification is micellar suspension. Putting raw CNT material into a solution of 1% surfactant and sonicating for several minutes will create a suspension of nanotube material that will stay suspended for weeks or months. There is evidence that the surfactant helps exfoliate the nanotube bundles, peeling individual CNTs off and suspending them in individual micelles[19]. However, it is unclear whether only nanotubes are suspended in the micelles, or whether the surfactant somehow removes non-nanotube carbon and metallic impurities. From AFM images (Figure 3-5) obtained of surfactant-treated nanotubes cast onto silicon substrates, it seems that both the CNTs and impurities are suspended. There may be other methods to separate the suspended impurities from the CNTs, such as centrifugation, but this is complicated by the fact that surfactant treatment may not be able to remove carbonaceous impurities from CNT walls. In addition,

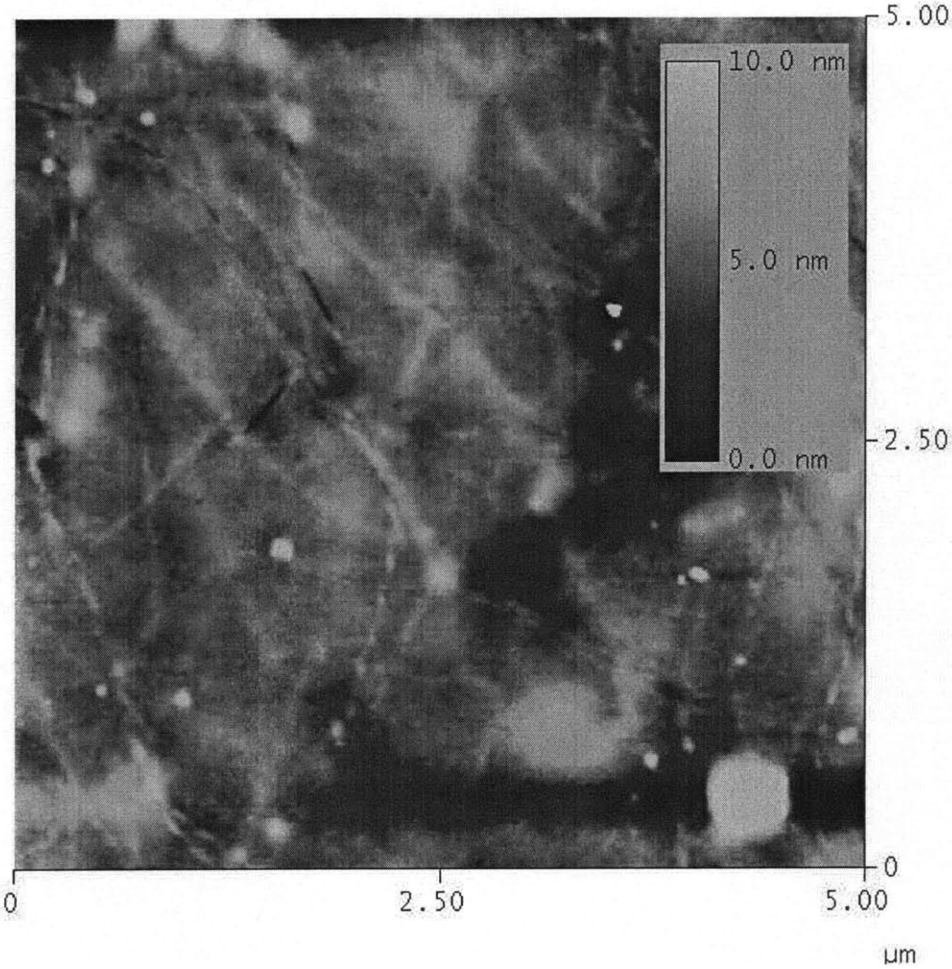


Figure 3-5: Raw arc-discharge SWNTs suspended in a 1% SDS solution, deposited on silicon.

the varying diameters and lengths of the CNTs make it difficult to segregate them from amorphous carbon in any physical way (e.g. mass, size, etc). The best purification solution may be a combination of several techniques.

3.3 Carbon nanotube separation

In order for purified CNTs to be used for electronic components, they will have to be separated by electronic properties, and perhaps also by diameter and length. Separating metallic from semiconducting CNTs is the first and most important task that must be overcome for device development. One possible method relies on the affinity of surfactant amines for semiconducting SWNTs. The reagent octadecylamine (ODA) was first used to modify SWNTs by Chen et al[20].

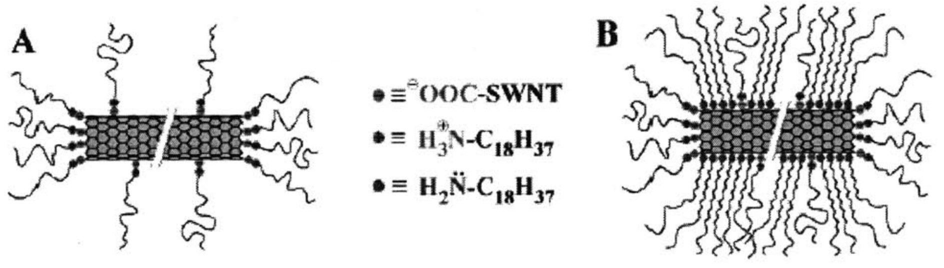


Figure 3-6: Octadecylamine is thought to coordinate to a CNT by ionic attraction to carboxyl groups at defects and electron transfer with the nanotube's π-orbitals[7].

This particular reaction will be discussed in more detail in a future section, but the essence of it is that ODA, in addition to forming a zwitterions with acid-treated CNTs, also forms a micelle around CNTs, stabilizing them in solution. This micellar interaction is apparently more favored for semiconducting CNTs. Thus, the semiconducting nanotubes are more strongly suspended, and precipitation via partial evaporation or centrifugation yields a supernatant rich in semiconducting CNTs, of up to 90% enrichment over the raw material. Even higher enrichments can be achieved for small-diameter SWNTs. There are several other separation schemes that involve modifying CNTs chemically. This is of particular interest to us because we intend to chemically modifying CNTs for other purposes. If we are able to also separate metallic and semiconducting CNTs simultaneously, that will reduce the overall complexity involved in processing CNTs.

Another method of separation relies on the difference in dielectric constants between metallic and semiconducting CNTs. By using an ac dielectrophoresis method, metallic CNTs in a mixed surfactant suspension can be attracted to the electrodes, leaving the semiconducting CNTs in the solvent. This process has been reported to yield an 80% enrichment in metallic CNT content relative to the raw sample[21].

Recent research has concluded that different nanotube growth methods produce different ratios of metallic and semiconducting CNTs. Li et al, in investigating SWNT growth by PECVD, discovered that over 90% of the nanotubes grown in this way are semiconducting. Tests on other materials show that HiPCO-grown tubes are ˜61% semiconducting nanotubes, and laser ablation grows ˜70% metallic nanotubes[22].

3.4 Summary

Carbon nanotube processing is a field in which a lot of work has been done. Three primary methods of nanotube growth are in use, with many variations possible. Ways to grow longer and more uniform carbon nanotubes are being researched. Current purification and separation techniques are at the point where successful CNT integration into macroscopic applications such as building materials is possible. In order for CNTs to be used in CMOS processes, more work will need to be done, not only in terms of growth, purification, and separation, but also in terms of patterning and assembly.

Chapter 4

Carbon Nanotube Interconnect Processing

Integrating carbon nanotubes into CMOS structures will require the adaptation of general CNT processing methods to the unique conditions of the CMOS environment. Unlike macroscopic applications, CMOS fabrication demands both accurate placement of features on the nanometer level and large, efficient batch processing. Current nanotube growth, purification, parameter-based separation, and placement technology must be refined extensively before becoming compatible with CMOS.

4.1 Integration via carbon nanotube direct growth

The ideal method for generating CNT interconnect structures on a surface would be via direct growth. By writing a specific pattern to a surface, then inducing CNTs to grow at specific points on that pattern, with specific directionalities and alignments, a complete system of CNT vias and horizontal interconnects could be quickly and efficiently produced. Unfortunately, this task is a lot more difficult than it sounds, because patterned CNT growth can only be achieved under certain conditions, some of which are still unknown.

As mentioned previously, CNT growth can be accomplished via arc-discharge, laser ablation, or chemical vapor deposition. Two potential concerns with direct CNT growth in a CMOS environment is the possibility of metal contamination from the catalyst and the high growth temperatures required. For nanotube growth, the kind of metal used for catalysis, as well as the temperatures and energies involved determine the type and quality of CNTs produced. MWNT growth has been demonstrated with no catalyst and at low temperatures, albeit of rather poor quality. SWNT growth requires much higher temperatures, from 800°C up, and the presence of a catalyst, usually iron (Fe) or nickel (Ni). Recently published papers have shown that plasma-enhanced CVD (PECVD) allows the growth of SWNTs at temperatures comparable to MWNT (600°C), but still requiring a metallic catalyst[22]. There are methods for growing SWNTs without metal catalysts, but in general they suffer from other advantages, such as low yield or extremely high process temperatures. Recently, NASA reported an arc-based growth method for high-quality SWNTs that does not require a metal catalyst[?]. Even if the need for metal catalysts in CNT growth cannot be circumvented, current CMOS techniques for isolating metal lines can be adapted for catalyst deposition. In addition, the published PECVD technique gives us hope that growth temperatures can be lowered enough to be compatible with CMOS processes without a significant loss in nanotube quality.

In all the growth methods, the as-grown CNTs are generally randomly dispersed and of random orientation and size. MWNTs have been grown on silicon oxide in well-ordered vertical clumps that can be well defined[8], but the same has not been achieved for SWNTs. However, researchers have found that SWNT growth directions can be influenced by electric, magnetic, and gravitational fields, as well as feedstock gas flow[16]. Another instance of directed growth of SWNTs has been reported by Dai et al at Stanford, which involves catalyzed growth from silicon oxide pillars[23]. The SWNTs grown in this way are suspended between different pillars, allowing a sort of directionality. It is also possible to catalyze CNT growth within another substance. Methods for growing SWNTs in the pores of a mesoporous alumina zeolite have been published, resulting in arrays of SWNTs of relatively uniform diameters and lengths[24]. The diameters of grown nanotubes depend on the size of the precursor catalyst particle. Most metal catalysts used today have random size distributions, leading to the growth of CNTs with different diameters. However, it is possible to synthesize nanoparticles with reasonably uniform diameters, and there is promising work in progress in this area. While it is generally accepted that higher growth temperatures result in higher-quality CNTs, it is not fully understood exactly what determines the quality of a grown CNT.

The fact that CNTs are grown in a relatively random fashion could impede any effort to harness their useful properties. For example, if current CNT growth techniques are used to fabricate a clump of MWNTs for a via, the nanotubes that comprise the via will have different numbers of shells and lengths. The length can be controlled to a certain extent by growth time and physical methods after growth, but the number of shells, and more importantly, the electronic properties of the as-grown CNTs will be fairly random. Theoretically, a third of any CNTs grown will be metallic or semi-metallic, and two-thirds will be semiconducting. Reports have shown that different growth methods yield different ratios of metallic to semiconducting nanotubes[22]; for example, CVD and HIPCO techniques tend to produce more semiconducting tubes, and laser ablation creates more metallic tubes. For a set of CNTs intended for interconnect purposes, inclusion of semiconducting CNTs could increase the resistivity of the structure unacceptably.

Some clarification must be given with regards to multi-walled CNTs versus single-walled CNTs. In general, in terms of sheer desirability, SWNTs are the nanotubes of choice for interconnect purposes. They are smaller in diameter than MWNTs - theoretically this means that more SWNTs can be packed in a given cross-sectional area than MWNTs. In general, only the outermost metallic shell of a MWNT will conduct, which means that all the shells of a MWNT contributes as much as the single shell of a metallic SWNT. Thus, SWNTs have essentially the same electronic characteristics as MWNTs, except they take up less space. One advantage of MWNTs is that if there is even one metallic layer in a MWNT, it will dominate the conductivity of the entire tube, and it is far easier to obtain a batch of MWNTs that all contain a metallic shell than a batch of entirely metallic SWNTs. However, as mentioned previously, there are methods to bias SWNT growth towards a predominance of metallic or semiconducting tubes, as well as to separate grown tubes by electronic properties. In general, MWNT growth gives much better structural and placement control, and is possible under more benign conditions. Thus, while SWNT interconnects is the eventual goal, MWNT interconnects may be more feasible in the short term.

The problems with the direct growth of CNT structures on a substrate are thus apparent. While it may be possible to use vertical MWNT clumps as vias, the random orientation, random properties, and high energies necessary to grow high-quality SWNTs render the direct growth method undesirable for directly fabricating SWNT vias or CNT lines in current CMOS technology.

4.2 Integration via carbon nanotube placement

Given that direct growth of CNTs in current CMOS technology is not feasible for most purposes, the alternative method for integrating CNTs into CMOS is by directed placement of grown nanotubes. This requires the external growth of CNTs and some method of attaching the CNTs to the substrate. The advantages of placement as opposed to direct growth include removal of the high-temperature CNT growth steps from the CMOS process and the possibility of processing the nanotubes prior to integration into the CMOS structure. In addition, placement introduces the possibility of attaching CNTs to a surface in an aligned and directed fashion. There are three major obstacles that must be overcome for the directed placement of CNTs for interconnects to be viable: purification, separation, and assembly.

As mentioned earlier, researchers have managed to grow vertical columns of well-ordered MWNTs at defined locations on silicon oxide. This is a possible pathway for building CNT vias. However, the majority of interconnects on a die are of the horizontal variety. If 3D chip architectures ever become commercially viable, this may change, but currently vias play a small role in the overall interconnect structure. Therefore, while using CNTs as vias would certainly be a major advance, using CNTs as horizontal interconnects could potentially revolutionize the CMOS industry.

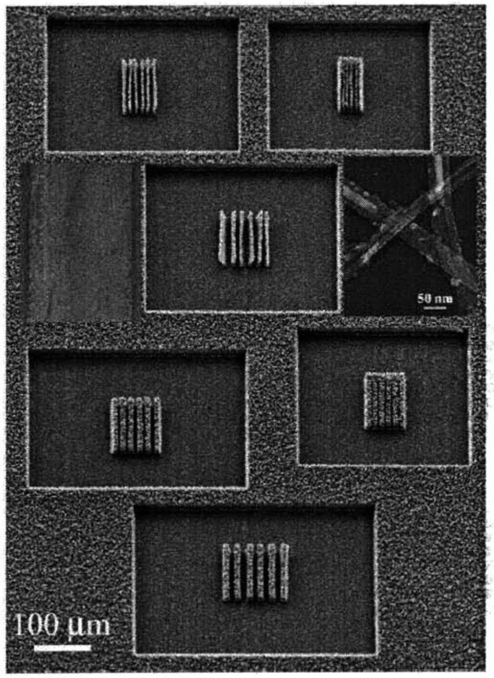


Figure 4-1: Vertical pillars of MWNTs grown by Ajayan's group at the Rensselaer Polytechnic Institute[8].

One of the biggest obstacles to horizontal CNT lines is the issue of placement. Current technology allows chip makers to lay down interconnects with pitches in the nanometer regime with a few processing steps. Contrast this to the state of the art in CNT technology: in order to fabricate a CNT field effect transistor, researchers need to spin-coat a suspension of nanotubes onto a substrate, use scanning probe microscopy to find a suitably isolated nanotube somewhere on the substrate, mark that particular tube, then lay down metal contacts. Clearly, this approach will not work for batch device or interconnect fabrication. What is needed is a way to define a position and orientation on a surface, then a way to place a nanotube at that position, with that orientation. Once this has been achieved, bulk placement of CNTs for both device and interconnect purposes will become much easier.

One method for the directed placement of CNTs utilizes the nanotubes' affinity for electron transfer. Researchers have shown that nanotubes are selectively attracted to a polar surface, and are repelled from a nonpolar surface[25]. Therefore, by adding a substrate patterned with specific polar and nonpolar regions to a suspension of CNTs, a pattern of CNTs conforming to the polar regions on the substrate can be generated. This particular group has demonstrated that individual CNTs can be confined to a thin region via these polar/nonpolar interactions.

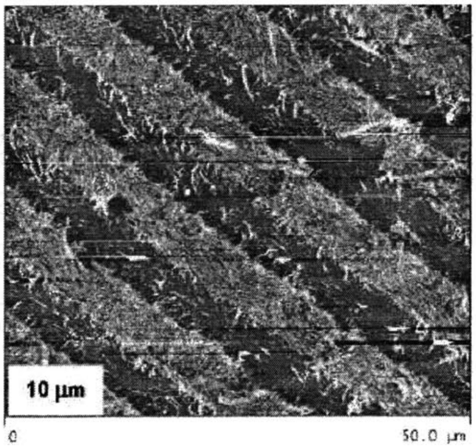


Figure 4-2: Carbon nanotubes adsorbed onto polar stripes[9].

Another possible method for directed placement of CNTs takes advantage of complementary group chemistry. If a nanotube is modified with a chemical handle that has a strong affinity to a complementary chemical handle on a surface, then the nanotube may selectively migrate to and bond with the handle on the surface. If a nanotube has a pair of handles, one near each end, there is only two ways it can bind to a pair of handles on a surface. Thus, precise positioning and directionality can be achieved.

There are three main obstacles that must be overcome for a viable complementary group-based directed placement process. First, there must be a way to attach the handle onto the CNT. Second, there has to be a way to attach the complementary handle to the surface in a desired pattern. Third, the complementary groups must be selected for the handle binding process.

4.2.1 Carbon nanotube chemistry

Chemistry involving carbon nanotubes have generated a lot of research interest, because CNTs are a novel material and may act as a reagent for new and useful chemical reactions. The single biggest obstacle to CNT chemistry is the fact that carbon nanotubes are not soluble in anything. Much of the existing body of known chemistry relies on chemical reactions in solution-phase. Since raw CNTs are generally insoluble, chemists cannot take advantage of the extensive chemical toolkit that solution chemistry provides, and must either look for other ways to manipulate and modify CNTs or find a way to make CNTs soluble. In addition to ease of chemistry, rendering CNTs soluble will also facilitate their integration into

CMOS processes. Currently, CMOS materials are incorporated into the integrated circuit via either deposition from gas phase (physical and chemical vapor deposition) or liquid phase (spin-coating). Clearly, grown nanotubes cannot be deposited via gas phase, and deposition via liquid phase requires solubility in order to achieve homogeneity.

It turns out that there are chemical methods to modify CNTs that are not in solution. The first reaction that generated modified CNTs was a fluorination that attached fluorine atoms to the nanotube sidewall. This was followed by other reactions utilizing activated carboxylic acids and noncovalent methods. Many of the products from these reactions are soluble in a variety of polar and nonpolar solvents, such as water, dimethylformamide and chloroform.

One of the reactions we investigated for the modification of CNTs is the octadecylamine (ODA) reaction mentioned earlier. This method relies on activating CNTs by transforming exposed carboxylic acid groups into acyl chlorides via the addition of thionyl chloride. Once the CNTs have been activated, they are mixed with ODA and heated. The resulting CNTs are reasonably soluble in a variety of organic solvents.

The problem with this reaction is that once the CNTs are modified, there are no other free functional groups that could act as handles for manipulation. To solve this, we modified the ODA reaction to use other reagents, in particular 1, 12-diaminododecane and 12-aminododecanoic acid. Unfortunately, we encountered problems with both reagents. The reaction with the 1, 12-diaminododecane resulted in a hard, insoluble black mass we theorize is due to cross-linking of the end amino groups to each other. The reaction with the

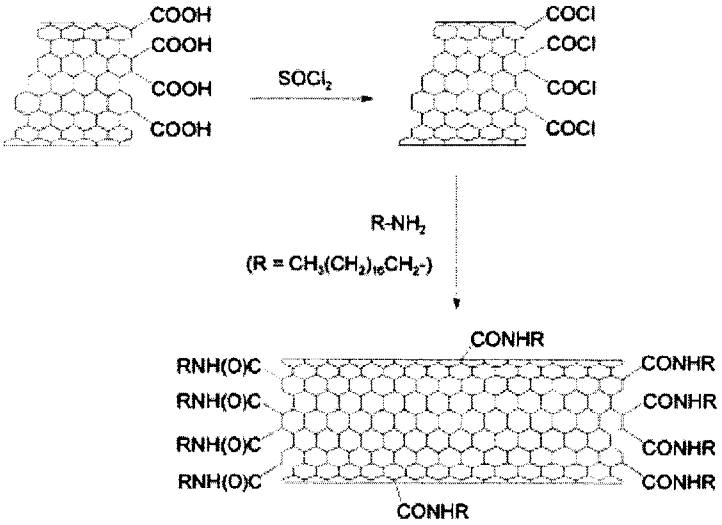


Figure 4-3: Functionalizing CNTs with octadecylamine (ODA). Treatment of carboxylic acids with thionyl chloride ($SOCl_2$) creates acyl chlorides, which react easily with amines. Theoretically, the R-group can be any desired moiety. Practically, there are other chemical constraints, such as side-reactions[10].

12-aminododecanoic acid, carried out at the high melting point of the acid (200?), instead resulted in condensation as the amine and carboxylic acid ends reacted with each other. These reactions may have produced the desired modified CNTs, but characterization of the products was not possible due to difficulty of handling them.

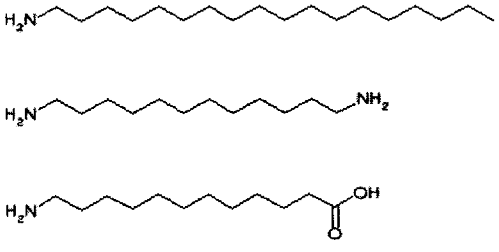


Figure 4-4: The three molecules we used for functionalization. In order, from top to bottom: ODA, 1,12-diaminododecane, 12-aminododecanoic acid.

Another method for CNT modification that we investigated was an aryldiazonium salt reaction first published by Tour et al in 2003[11]. This reaction is thought to be based upon electron transfer between micelle-suspended CNTs and the aryldiazonium salts, and produces CNTs soluble in dichlorobenzene, DMF, chloroform, and tetrahydrofuran (THF). We reproduced this reaction using a single diazonium salt, 4-nitrobenzenediazonium tetrafluoroborate, and obtained a black solid soluble in DMF. AFM images of the product reveal what appear to be individual CNTs, as well as significant amounts of impurities. Further work will need to be done to reduce the amount of impurities in this process, perhaps by thermal or other chemical purification techniques applied to the starting material.

The modified CNTs we obtained from the aryldiazonium reaction are terminated with nitro groups, since the starting salt was a nitrobenzenediazonium salt. In order to use these

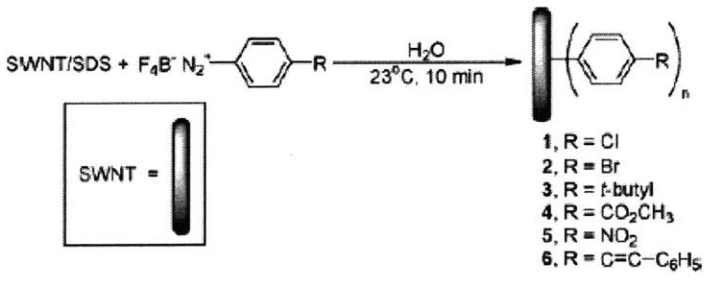


Figure 4-5: The diazonium salt reaction, first used to modify nanotubes by Tour et al (cite). The reaction mechanism is thought to be radical-based, with the CNT donating an electron to the salt, evolving nitrogen gas and a highly reactive radical that then attacks the nanotube sidewall[11].

CNTs in the directed-assembly process we had envisioned, we needed to alter the nitro group into something that we could use. We eventually settled on a nitro reduction reaction using tin chloride that reduces the nitro group to an amine group[26]. The original reaction takes place in an aqueous medium. However, the diazonium-modified CNTs are only soluble in DMF and other organic solvents. We decided to try to adapt the original reduction reaction for use in DMF. The product of the adapted reaction was at first insoluble in water, but after addition of HCl part of the product went into solution. AFM images of the colored solution reveal a few scattered tube-like structures and a lot of impurities.

4.2.2 Surface chemistry

Once CNTs with the desired chemical handles have been obtained, the next step is to bind these handles to a surface in a targeted fashion. One method might be to rely on surface-handle group interactions. For example, it is well-established that thiol groups (sulfur and

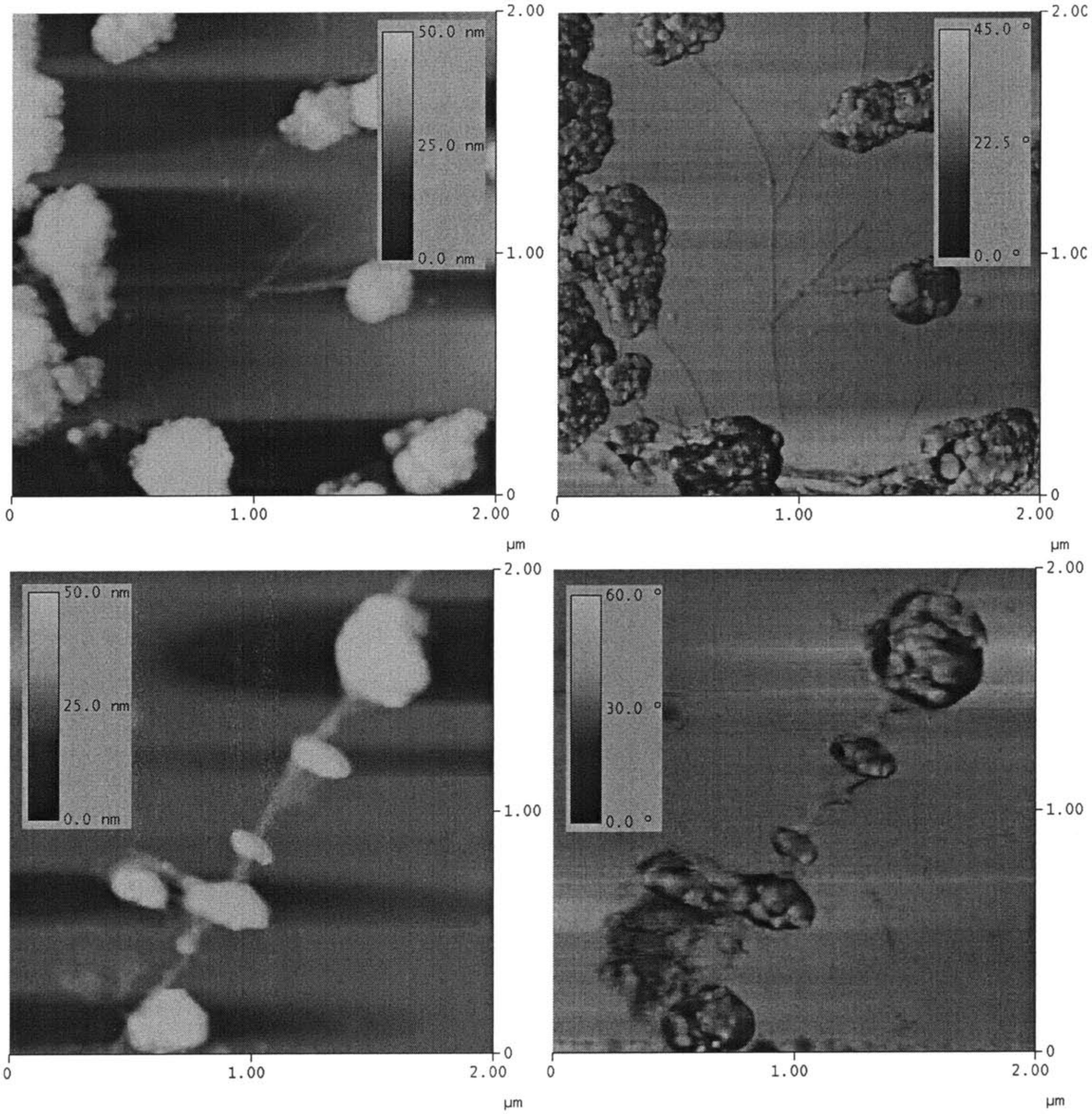


Figure 4-6: Tapping-mode atomic force microscope height and phase images of raw nanotubes (bottom) and nitrobenzene-modified nanotubes (top). The modified CNTs are less prone to bundling compared to the raw nanotubes. Both samples were cast from dimethylformamide.

hydrogen) will bind strongly to gold. If a gold pattern is defined on a surface, perhaps by lithography, a solution of CNTs modified to have thiol handles should selectively bind to the gold regions. Another method is to use handle group-handle group interactions, with the modified CNTs binding to a pattern of complementary molecules on a surface. This surface pattern can be created by selective growth of a self-assembled monolayer (SAM). A self-assembled monolayer is composed of a group of homogeneous molecules that are attracted to a surface. When these molecules bind to the surface, they rearrange to reach a minimum energy configuration, usually as a relatively uniform layer a single molecule thick. These self-assembled monolayers can be patterned in a number of different ways. The simplest method would be a lithographically defined pattern, similar to the one discussed above, except instead of using modified CNTs, SAM molecules would be used. Other methods that may result in better resolution include dip-pen nanolithography[27] and replacement nanolithography[28]. For our purposes, the SAM molecule used must be able to bind to the surface on one end and to a modified CNT on the other end. Once a monolayer is grown in the desired pattern, the substrate can be immersed in a solution of modified CNTs, and self-assembly will occur.

4.2.3 Carbon nanotube placement methods

In order for the self-assembly process to occur, we must effect some sort of binding mechanism between the CNTs and the substrate. First we must decide what the form of the bond should be. For example, we could attach a handle group to the nanotube and have that handle group interact with the surface, or vice-versa. There could be handle groups on both the nanotube and the surface that interact with each other, or with another separate linker molecule. Then we must consider the actual bonds used. There are two chemical interaction types that are feasible. The first type is a noncovalent linkage, such as van der Waals or ionic interactions. The second type is a covalent bond that actually shares electrons between the two participating groups.

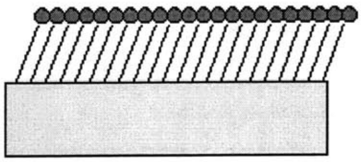
Noncovalent interactions are easier to induce, but are unstable compared to covalent bonds. Examples of noncovalent interactions include the van der Waals attraction of graphene layers to form graphite and the ionic bonding of sodium and chlorine atoms to form table salt. These bonds can be readily broken; graphene layers can be easily exfoliated by shear force, demonstrated by the use of a pencil, and table salt dissolves quickly in water, dissociating into its component sodium and chloride ions. However, noncovalent bonds can be strong as well; note the difficulty in separating CNT bundles, which are held together by van der Waals interactions.

In general, noncovalent interactions involving CNTs take place via one of two mechanisms: pi-pi stacking and electron transfer. An sp2 hybridized carbon atom has a third pi orbital that extends perpendicular to the sp2 plane. In a molecular structure with a number of sp2 carbons bound to each other, such as benzene, graphene, or a carbon nanotube, the presence of the multiple overlapping third pi orbital enables an electron delocalization effect. The phenomenon of pi-pi stacking occurs when the delocalized pi orbitals of two or more of these "aromatic" structures intersect each other, like plates stacked upon each other, and results in a stronger electron delocalization and a significant attractive force. Carbon nanotubes, with their extremely large delocalized pi orbitals, are also excellent electron acceptors. Thus, a strong noncovalent interaction can be formed if a donor-type molecule transfers an electron to a carbon nanotube. (need examples) The noncovalent-type bond is appropriate for nanotube-handle group, surface-handle group, and handle group-linker interactions.

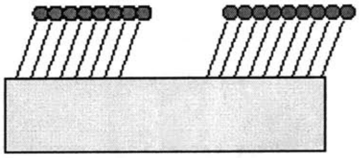
The other bond type is a covalent bond, in which two chemical groups share electrons. The covalent bond is the strongest chemical bond known, and is capable of facilitating electrical conductivity under certain conditions. While covalent bonds are far more stable than noncovalent interactions, forming covalent bonds directly to carbon nanotubes will probably result in degradation of the CNT electronic properties, as mentioned earlier. As with noncovalent interactions, covalent bonds are suitable for surface-handle group, handle group-linker, or handle group-nanotube interactions. In an electronic sense, it may not be as desirable for direct links to CNTs.

The first bond architecture we are considering is a noncovalent interaction between unmodified CNTs and a patterned polar/nonpolar SAM (Figure 4-7). First published by (x), this simple process involves creating a monolayer pattern of polar ligands, backfilling with nonpolar ligands, and then evaporating a suspension of CNTs onto the substrate. The CNTs selectively adhere to the polar regions, and are actually repelled from the nonpolar regions.

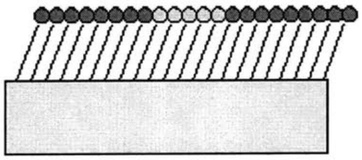
Another method we are investigating relies on a covalent interaction between modified CNTs and a monolayer (Figure 4-8). In this case, we are trying to form an amide linkage



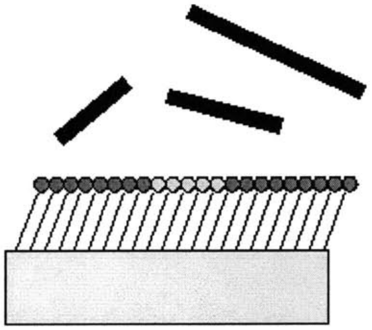
1) self-assembled monolayer growth



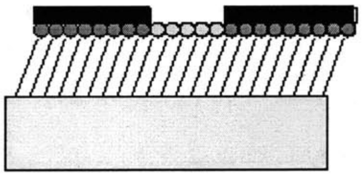
2) SAM patterning



3) backfill with nonpolar ligands



4) add unfunctionalized CNTs



5) CNTs stick to polar ligands

Figure 4-7: The noncovalent pattern process. After the polar monolayer is initially grown, the ligands are removed in a certain pattern, and a nonpolar ligand is used to fill in the pattern. The unmodified CNTs are added and assembly onto the polar regions. Alternatively, the nonpolar ligands can be patterned first.

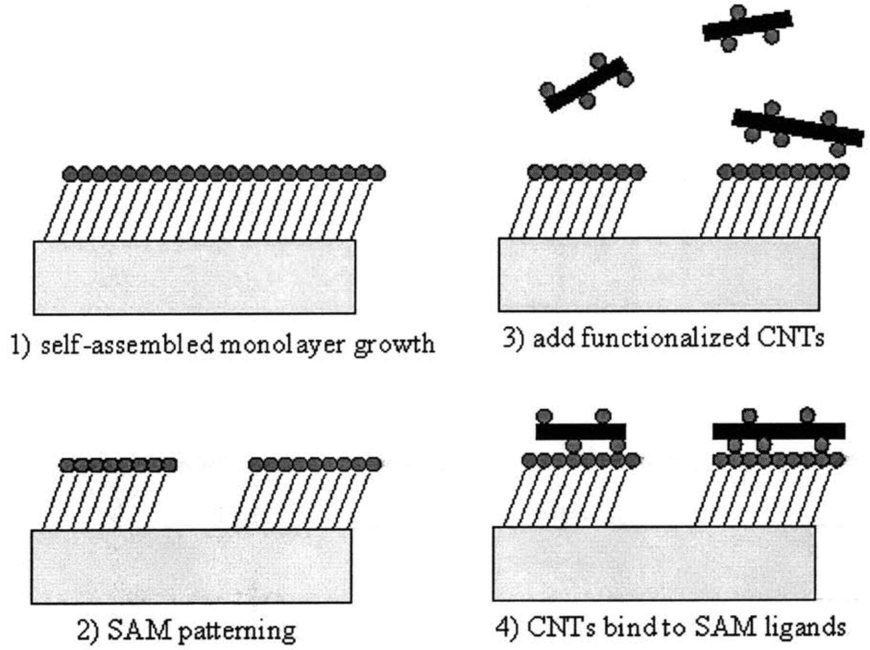


Figure 4-8: The covalent assembly process. The first two steps are similar to the noncovalent process, and in fact a neutral ligand could be used to backfill the empty areas. Modified nanotubes are then added, and the substrate treated to promote bond formation between the groups on the nanotubes and the surface ligand groups. This treatment could be anything from heat and light to another catalyzing reagent.

between the nanotube handle groups and the surface monolayer ligands. An amide bond, also known as a peptide bond, is formed by the removal of water from an amine group and a carboxylic acid group. Formation of amide bonds can be extremely time-consuming, and is usually facilitated by the use of a catalytic reagent such as dicyclohexylcarbodiimide (DCC). Unfortunately, use of these DCC and other such reagents require absolutely dry conditions (no water), and this is difficult to achieve with our CNT and monolayer processes. An alternative that is under consideration is the use of a prepatterned polymer stamp to accelerate the reaction rate[29].

4.3 Carbon nanotube interconnect structures

Once directed CNT assembly has been achieved, the next step is to move to a true CNT wiring scheme, which requires massive interconnection of multiple individual nanotubes. It is theoretically possible that some method can be devised to route a long nanotube or nanotube bundle between devices, but currently the most efficient approach may be to lay down nanotubes in the desired pattern and connect them to each other via some other method. This method can range from using metal contacts to somehow coaxing the individual nanotubes into growing together. The simplest technique is to just lay down metal contact strips between the separate nanotubes. This can be done via standard CMOS metal deposition techniques, such as PVD or electron beam evaporation.

Early attempts at fabricating CNT devices encountered high resistances between the metal contacts and the nanotube, anywhere from kΩs to MΩs. Further attempts with different metal types have decreased CNT structure resistances, with palladium quickly becoming the metal of choice, and measurements at low temperatures, around 4K, have approached the ideal 6.45 kΩ mark. However, the true nature of the metal-nanotube contact is not fully understood yet - there are several factors that could affect the quality of the metal-nanotube contact, such as metal deposition conditions or resistance to oxidation.

4.4 Summary

In order to integrate carbon nanotubes into CMOS technology, methods for handling CNTs precisely and accurately must be developed and refined. Currently, CNT structures can be generated on silicon via either direct growth or placement. We are attempting to further refine existing placement processes by integrating complementary group chemistries to selectively bind SWNTs to a surface with specific alignments. More work will also need to be done to characterize the exact nature of the metal-nanotube interface in order to minimize contact resistances.

Chapter 5

Carbon nanotube thermal applications in CMOS

5.1 CNTs and thermal issues in integrated circuits

Carbon nanotubes, with their potentially useful electronic properties, could represent a future generation of CMOS interconnects. However, benefits from the excellent thermal characteristics of carbon nanotubes should not be overlooked. As technology generations advance, getting rid of excess heat generated by operating devices will become critical. Designers are always trying to fit more active devices in a given area and to switch them faster, and temperatures will rise as device density and switching speed increase. If steps are not taken to alleviate this thermal distress, at some point devices will shut down because of extreme temperature. Currently, heat removal is accomplished via thermal conduction through bulk silicon to an external heat sink, which dissipates heat with the help of a fan or a liquid cooling unit. While this one-dimensional method is adequate for the present, it will not be able to remove heat quickly enough from future highly integrated circuits. In particular, if three-dimensional circuit architectures ever become widespread, heat removal methods that use as much of the reduced surface area will be necessary. There are several alternatives that are being pursued; one of the most promising uses fluidic microchannels within the CMOS structure to carry heat away from active devices laterally. Another possible solution could be to use carbon nanotubes, with their extremely high thermal conductivities, as thermal channels.

The biggest advantage carbon nanotubes have with respect to heat dissipation is clearly their superior thermal conductivity. With conductivity values possibly exceeding those of diamond and graphite, which are in turn an order of magnitude greater than most metals, a heat removal system incorporating CNTs as heat pipes could channel heat out of integrated circuits very efficiently. In addition, if CNT interconnects become widely used, the interconnect structure could also serve as a framework for heat dissipation.

The problem with a CNT-based thermal management solution is the same reason CNTs are potential interconnects: they are ballistic transporters with good electronic properties. Ideally, the best material for heat dissipation would have a high thermal conductivity and be a good insulator. Metals, which are very thermally conductive, are not used as heat channels within an integrated circuit because they are electrically conductive and would cause signal loss and interference. Unlike metals, thermal transport in CNTs is dominated by photons[15]. Thus, good thermal conductivity is possible without good electrical conductivity. If CNT structures can be engineered so that thermal transport is maximized while leakage currents are minimized, then CNTs could be a viable heat removal method.

In terms of the current two-dimensional circuit architecture, any possible contributions CNTs could make to thermal management is by enhancing thermal conductivity into the bulk silicon and towards the heat sink. However, the bottleneck to heat removal in 2D integrated circuits is the heat sink, more precisely the thermal transfer to the heat sink and the subsequent transfer to air. Therefore, it is unlikely that any form of CNT integration into the CMOS structure could provide a significant enhancement to heat removal.

Another potential thermal problem is the effect of thermal gradients on circuit performance. In a given integrated circuit layout, there are generally regions where active devices are segregated, in order to shorten interconnect lengths and thus delays between devices. One of the consequences of this segregation is that the temperature profile of the circuit peaks in these device regions and drops off in areas with fewer devices. This will not only degrade device performance and reliability in these device-rich regions, but also cause timing mismatches between interconnects in high-temperature areas and those in relatively cooler sections[3].

One solution to this problem is the introduction of a dielectric with high thermal conductivity. While this would not help the overall IC thermal situation, it would help flatten the thermal profile and alleviate timing mismatch problems. If carbon nanotubes could be integrated into currently used dielectrics, high thermal conductivities could be achieved.

5.1.1 Carbon nanotube-enhanced dielectrics

Some of the key parameters of a CNT-dielectric composite are its thermal conductivity, electrical conductivity, and dielectric constant. A high thermal conductivity is desired, since the anticipated purpose of the composite is for efficient heat spreading. Electrical conductivity and dielectric constant values should not be high enough to induce leakage currents or undesired coupling between adjacent lines and devices. As the percentage of carbon nanotubes in a CNT composite increases, the thermal conductivity of the composite should also increase. However, once the CNT loading exceeds a certain percentage, a percolation network is formed throughout the composite matrix, and both thermal conductivity and electrical conductivity increase dramatically. This question then becomes: can a composite with CNT loading below what is required for a percolation network provide a significant increase in thermal conductivity? If not, is there a way to increase the electrical resistivity of a percolating CNT composite without decreasing its thermal conductivity?

Some simple simulations involving nanotube-oxide composites were done. Figure 5-1 is a simulation of the thermal conductivity of a hypothetical CNT-oxide composite. As expected, as the percentage of CNT content and the nanotube thermal conductivities increase, the overall thermal conductivity also increases. The CNT thermal conductivity was varied in this simulation to account for experimental uncertainty about the practical thermal conductivity of carbon nanotubes and alignment within the matrix. While the theoretical maximum thermal conductivity of a CNT is thought to be 6600W/m K at this time[14], actual nanotubes may have lower conductivities. In addition, we expect that as CNTs become more aligned in a matrix, their contributions in terms of thermal conductivity will become higher. Thus, varying the nanotube thermal conductivity addresses both of these issues, albeit in a simplistic fashion.

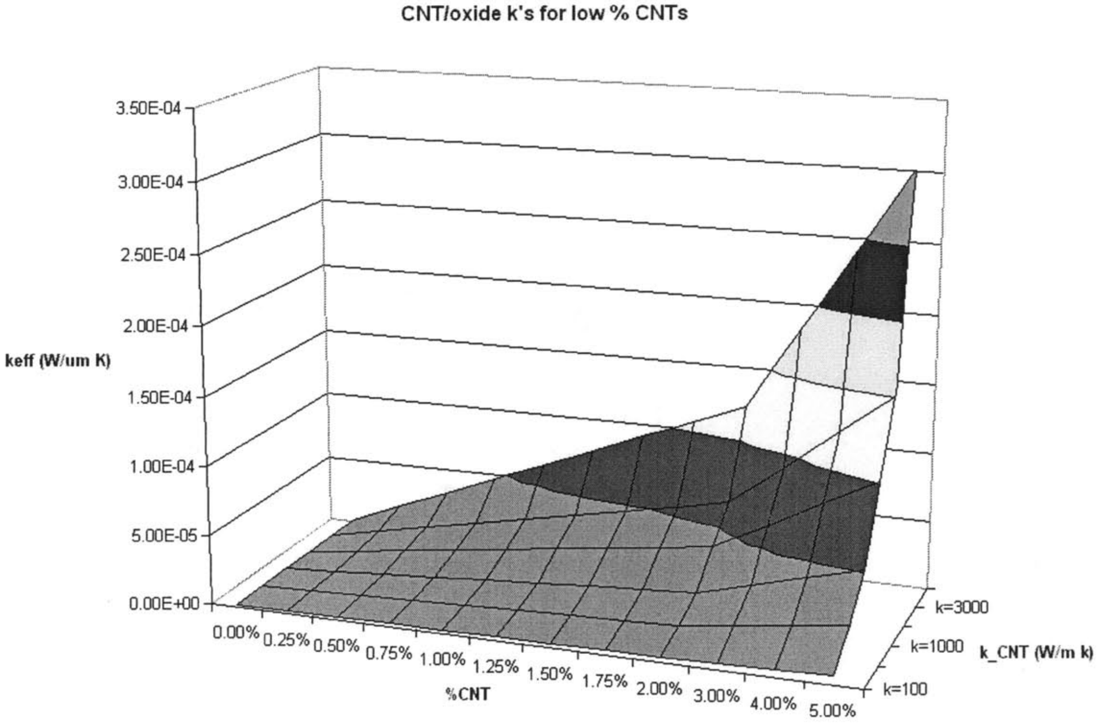


Figure 5-1: Simulation of composite thermal conductivity versus percent CNT loading and CNT conductivity. The formula used was %CNT$\times k_{CNT}$ + (1−%CNT) $\times$ k_{oxide}, where k_{CNT} and k_{oxide} are the thermal conductivities of the CNTs and the oxide, respectively. The values of k_{CNT} used were 100, 500, 1000, 2000, 3000, and 6000 W/m K.

Figure 5-2 shows a thermal simulation for a simple one-dimensional CMOS silicon-on-insulator (SOI) structure, where the buried dielectric is a CNT-oxide composite. Problems with creating a buried CNT-oxide composite aside, we see that the difference between the "junction" and "ambient" temperatures decrease significantly as the percent CNT loading and the CNT thermal conductivity increases. It must be noted that the "ambient" temperature in this situation is the temperature in the bulk silicon near the oxide; if this simulation is expanded to include the interface between the silicon bulk and the heatsink, the improvement in temperature gradient introduced by the CNT-oxide becomes insignificant. Thus, we concluded that the heatsink is the thermal bottleneck, and using CNT-oxide is not likely to improve heat removal from conventional 2-D integrated circuits.

Figure 5-3 is a simulation of temperature difference in a simple shallow trench isolation (STI) structure, where the trench dielectric is a CNT-oxide. Once again, as expected, the higher the CNT loading percentage and the nanotube conductivity, the smaller the temperature difference is between the two junctions.

We conclude from these simulations that any proposed heat removal method for CMOS technology has to address the bottleneck that the heat sink presents; however, temperature gradients within a circuit can be reduced if enhanced thermal conductivity dielectrics such as CNT-oxides are introduced.

5.1.2 Fabricating CNT-composite dielectrics

CNT-based composites have been investigated for mechanical and thermal applications in mechanical engineering. Biercuk et al[30] developed a simple CNT-epoxy composite that displayed improved thermal conductivity, with up to a 100% increase over the pure epoxy. Along the same lines, DiMaio et al[31] published a paper on the synthesis and optical properties of a CNT-silicon oxide composite.

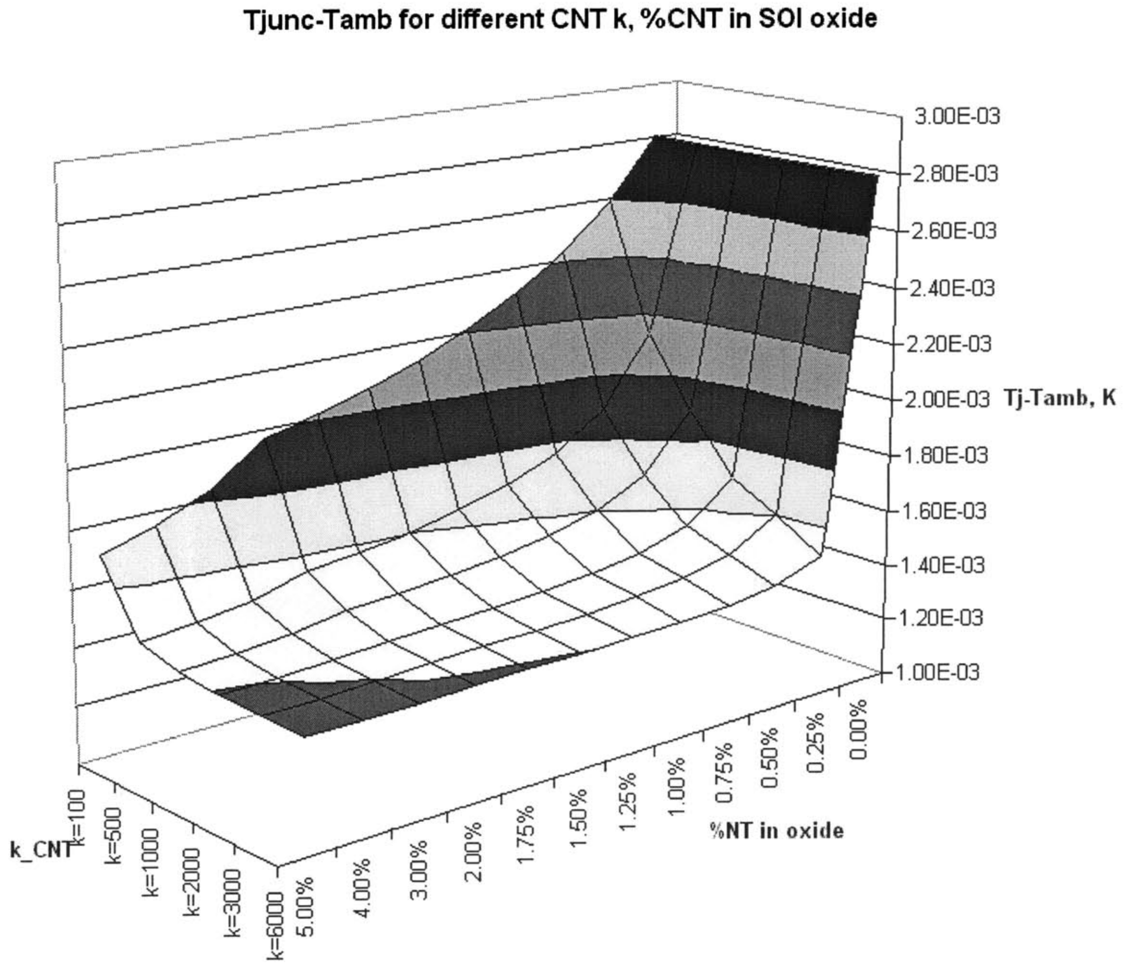


Figure 5-2: Simulation of the temperature difference between a "junction" and an "ambient" separated by a 0.3 μm layer of buried CNT-oxide. Power dissipation at the "junction" was 2 nW/μm^2. The "ambient" temperature was 300K.

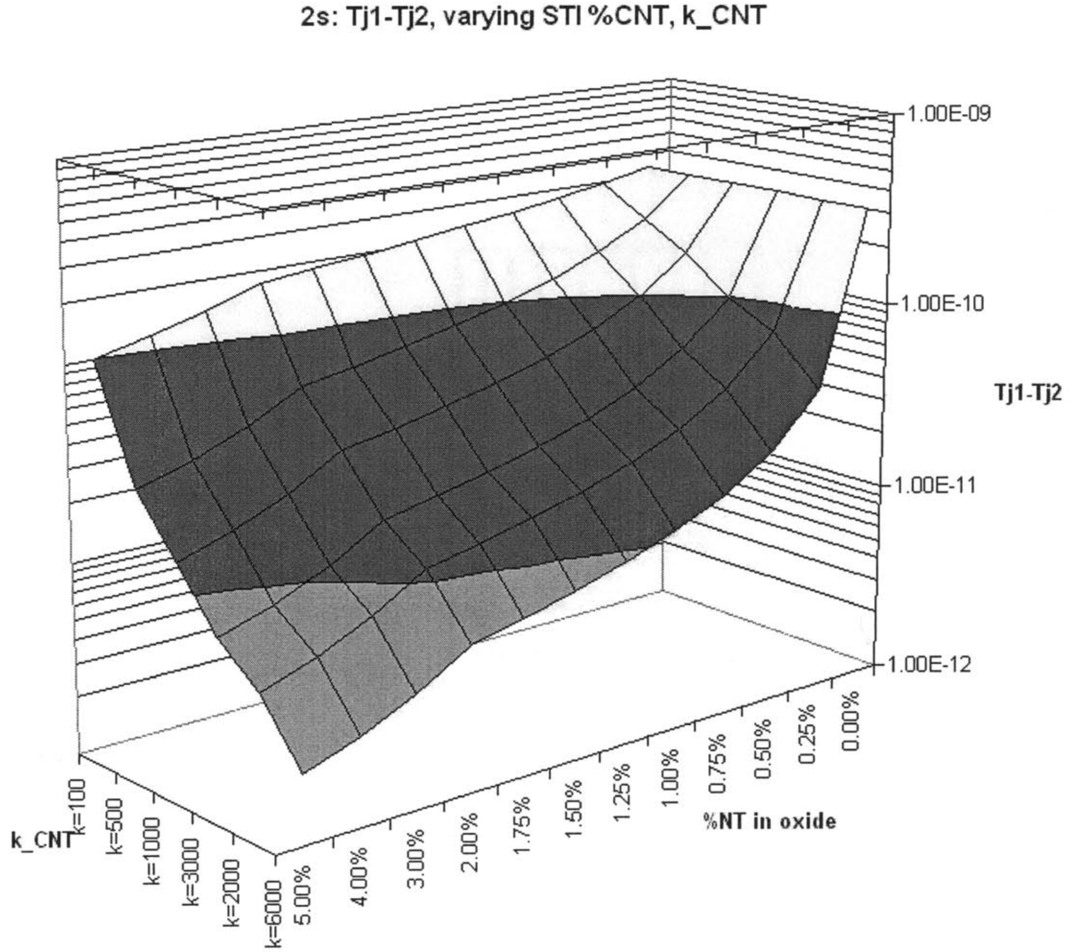


Figure 5-3: Simulation of temperature difference between two junctions in a 0.3 μm STI structure. One junction dissipates 2 nW/μm^2; the other junction dissipates 1 nW/μm^2. The "ambient" temperature was 300K.

We are currently attempting to fabricate CNT-oxide composites via a sol-gel technique Professor Ballato at Clemson University communicated to us. The heart of the sol-gel concept lies in a chemically-assisted transformation of a silicate liquid into a silicate gel. This gel is then thermally treated in order to dry and sinter the sample into a solid oxide structure. The biggest benefit of the sol-gel technique is that it starts with liquid precursors, which allows the incorporation of other substances into the eventual oxide matrix in a relatively simple fashion. In addition, the sol-gel liquid can be easily molded into monoliths or spun onto substrates to form oxide films. However, sol-gel does not compare favorably with current CMOS oxide growth techniques, primarily because of the complex procedures needed to form the sol-gel oxide.

In the original paper, raw carbon nanotubes were dispersed in the sol-gel precursor solution after they had been modified with I_{PEG}, an alcohol modified with polyethylene glycol. We intend to use either surfactant-suspended nanotubes in water or amine-modified nanotubes, which are soluble in water at low pH. In addition, we will investigate methods of aligning CNTs in the liquid precursor, either via magnetic or electric field application.

5.2 Summary

Carbon nanotubes have excellent thermal properties which can be utilized in CMOS applications. Instead of focusing on heat removal in conventional integrated circuits, which is limited by the heat sink, we are focusing on the thermal gradients within a die, which can lead to timing mismatches. By using CNT-composite dielectrics for shallow trench isolation purposes, we hope to alleviate these thermal gradients and reduce timing problems. The CNT-oxide composites are fabricated via a sol-gel technique, which is a versatile method of oxide formation.

Chapter 6

Conclusion

6.1 Summary

In this thesis, we have presented some of the possible applications carbon nanotubes may have in CMOS back-end technology. Their superior electronic and thermal conduction properties make them an attractive candidate for next-generation interconnects and thermal management solutions. Before commercial CNT deployment in CMOS, several issues have to be resolved. The first and perhaps most important is whether future CNT interconnects will be grown or deposited. The technologies involved in both techniques are still immature at this point in time, but future work in the areas of nanotube growth and manipulation should reveal the optimal solution. In addition, CNT purification, parameter control, and contact issues will need to be refined before nanotube interconnects can compete with the current copper technology. In terms of CNT-based heat removal applications, work needs to be done on fabricating CNT-dielectric composites with greater nanotube purity and alignment, and the thermal conduction, electrical resistivity and dielectric parameters of these dielectrics will need to be characterized.

6.2 Other CMOS applications for carbon nanotubes

The extraordinary versatility of carbon nanotubes in terms of electronic properties may usher in a new age of nanoelectronics. Conventional CMOS-based circuit structures are composed of a device layer fabricated nearest the bulk silicon wafer, with the supporting interconnect structure built farther away. Since carbon nanotubes can be both metallic and semiconducting, a circuit architecture composed of solely carbon nanotubes is not inconceivable. In addition, such an architecture would not be limited to the device layer-interconnect structure. The active-device nanotubes could be scattered throughout the entire interconnect structure in a three-dimensional sense, introducing new methods for circuit layout. The first step toward such a vision is the *active interconnect*, a nanotube wire with switching capabilities. A CNT interconnect deposited or grown on a substrate can be chemically modified *in situ*, altering its electronic properties or giving it switching capabilities. If an entire interconnect structure can be fabricated this way, an FPGA-like architecture would result. It is only a small step from this to replacing the CMOS-based transistor with nanotube transistors, thus producing an entirely nanotube-based architecture and introducing the possibility for novel circuit applications. Of course, the basic problems of nanotube growth, purification, and manipulation must be solved first, but with the amount of research being devoted to carbon nanotubes worldwide, we are confident that this is achievable.

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