Investigation on In-situ Growth of Carbon Nanotube Network by Chemical Vapor Deposition for Electrical Interconnect Applications

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ABSTRACT

According to Semiconductor Industry Association (SIA), global sales of semiconductors reached $247.7 billion in 2006, an increase of 8.9 percent from the $227.5 billion reported in 2005. Due to the increasing consumer demand for smaller computers that process data at a much faster rate, processors that have a large number of transistors and interconnects per chip are required.

For more than 40 years, the semiconductor industry has been able to improve the performance of electronic systems by doing continuous miniaturization or scaling of electronic devices that has led to faster and denser circuitry. This trend has resulted in feature sizes with nanometer dimensions. However, microelectronic device miniaturization will soon encounter a number of scientific and technical limitations. One example of these limitations can be found in copper as electrical interconnects. As interconnect feature sizes shrink, copper resistivity increases due to surface roughness and grain boundary scatterings. The microelectronics industry is exploring a number of alternative device technologies. One of the approaches is to use other materials to replace copper.

Carbon nanotubes are a promising candidate to create electronic interconnects for microprocessors due to their low resistivity at nanometer scale, resulting in being able to achieve high current density. Carbon nanotube network (CNN) interconnects were grown between gold electrodes 30 μm apart supported on Si/SiO₂ by combining micropatterning with the controlled growth of carbon nanotubes using nickel catalyst particle placement and a five gas-based CVD reaction. Electrical characterization showed metallic behavior
of the carbon nanotube network with a resistance of 281.05 kΩ (droplet method), 0.47 kΩ (in-situ, line), and 107.07 kΩ (in-situ, circle).

The resistances of the resulting carbon nanotube network interconnects are greater than the resistances of other interconnects reported in literature (Table 4). The possible reason of this is the geometry of each interconnect. In carbon nanotube network interconnect, there are lots of nanotubes overlapping each other, creating a network. Therefore, the resistance of that nanotube network is greater compared to that of carbon nanotube bundle and single-carbon nanotube interconnects.
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1.0 INTRODUCTION

Based on Semiconductor Industry Association (SIA) report [1], global sales of semiconductors reached a record $247.7 billion in 2006 (Figure 1). Microelectronic devices and technology have experienced a productivity development for more than 40 years. The semiconductor industry has been continuously doing miniaturization of electronic devices that has led to faster and denser circuitry (Figure 2) [2]. This trend has resulted in feature sizes with nanometer dimensions.

Figure 1: 25 years of chip sales [1]
Figure 2: Moore’s law – based on lateral scaling. Microelectronics will develop into nanoelectronics [2]

However, microelectronic device miniaturization will soon encounter a number of scientific and technical limitations. One example of these limitations can be found in copper as electrical interconnects. As interconnect feature sizes shrink, copper resistivity increases due to surface roughness and grain boundary scatterings (Figure 3 [3] and Figure 4 [2]).
Figure 3: Effect of miniaturization on Cu resistivity [3]

Figure 4: Illustration of electron scattering in small (nanoscale) Cu wires [2]
Carbon nanotubes are hollow cylinders composed of one or more concentric layers of carbon atoms in a honeycomb lattice arrangement (Figure 5) [4]. Most of literature attributes the ‘discovery’ of carbon nanotubes to Sumio Iijima of NEC in 1991. However, carbon nanotubes have been synthesized and observed prior to 1991. Oberlin, et al. [5] observed hollow carbon fibers with nanometer-scale diameters. These authors also show a TEM image of a nanotube consisting of a single wall of graphene. Later, Endo has referred to this image as a single-walled nanotube. Carbon nanotube research accelerated greatly following Iijima’s ‘discovery’ of single-walled carbon nanotubes and methods to specifically produce them by adding transition-metal catalysts to the carbon in an arc discharge [6].

Due to their excellent mechanical (i.e., high tensile strength; comparable to diamond – with Young’s Modulus of 1-1.2 TPa [7]) electrical (i.e., resistivity comparable...
to nickel-chromium on the order of $10^{-6} \ \Omega\cdot m$ [8]), and thermal (e.g., thermal conductivity exceeding that of diamond by a factor of two at greater than 3000 W/m-K [9]) properties, carbon nanotubes have been the object of intense scientific research to make improvements in many applications such as field emission devices (FED) [10], field-effect transistors (FET) [11], and electrical interconnects [12, 13].

According to Semiconductor Industry Association (SIA), global sales of semiconductors reached $247.7 billion in 2006, an increase of 8.9 percent from the $227.5 billion reported in 2005 [14]. Semiconductor devices are widely used in digital systems (such as computers and calculators). For more than 40 years, the semiconductor industry has been able to improve the performance of electronic systems by doing continuous miniaturization or scaling of electronic devices that has led to faster and denser circuitry. This trend has resulted in feature sizes with nanometer dimensions. However, microelectronic device miniaturization will soon encounter a number of scientific and technical limitations. One example of these limitations can be found in copper as electrical interconnects. As interconnect feature sizes shrink, copper resistivity increases due to surface roughness and grain boundary scatterings [15,16,17].

The microelectronics industry is exploring a number of alternative device technologies. One of the approaches is to use other materials to replace copper. Carbon nanotubes are a recently discovered form of carbon which can be thought of as a rolled-up sheet of hexagonal ordered graphite formed to give a seamless cylinder. Carbon nanotubes have some unique properties (mechanical, electrical, and thermal – as described before), which make carbon nanotubes a promising candidate for replacing copper as interconnects [18].
One of the main problems with using carbon nanotubes as interconnects is the manufacturability of the devices. The techniques used to fabricate carbon nanotube-based interconnects are only applicable in laboratory-scale experiments, not in an industrial scale. This is because of the limited number of interconnects fabricated with those techniques per unit time. It is important to investigate a new method to fabricate electrical interconnects efficiently. *In-situ* growth of carbon nanotubes is a method to fabricate multiple interconnects at once. Therefore, it is a way to solve the problem related to the manufacturability of carbon nanotube interconnects.
2.0 CRITICAL LITERATURE REVIEW

The history of metal-oxide-semiconductor field-effect transistor (MOSFET) starts as early as 1964 when the first MOSFET was invented. Since then, this device has dominated digital applications such as computers. MOSFET offers high reliability and low power consumption. It can also be packed in large numbers within a single integrated circuit due to its relatively small size. MOSFET is a device that has three terminals which are gate, source and drain terminals. The gate controls the current flow from source to drain.

As the gate voltage is raised above the threshold voltage, an inversion layer or channel is created and hence electrons will flow from source to drain terminal and current flows from drain to source terminal. There is no current flow to gate terminal since there is an oxide barrier that acts as insulator. Figure 6 shows the structure of MOSFET [19].

![Schematic diagram of MOSFET](image)

**Figure 6: Schematic diagram of MOSFET [19]**

Scaling is a process of reducing the size of MOSFET. The first method was introduced in 1974 in which by reducing the MOSFET dimension, the device density and
switching speed are improved. Figure 7 shows the growth in the number of transistors per chip over the past 35 years [20].

![Figure 7: Growth in the number of transistors over the past 35 years [20]](image)

The trend of this miniaturization is known as “Moore’s Law”, initiated by Gordon Moore, the Intel’s co-founder. It is predicted that the number of transistors in integrated circuit will double every 18 months. However, as the size of MOSFET continues to decrease even further, there are some limitations regarding this miniaturization, due to the fact that there are several factors that could affect the performance of MOSFET as its size becomes too small (i.e., in nanometer dimensions).

### 2.1 Limitations to MOSFET Scaling

There are several effects that appear as the MOSFET size reaches nanometer scale. These will become the limiting factors that affect the performance of the MOSFET itself. The factors are short channel effect, tunneling effect, and threshold voltage.
Short-channel effect is a notable effect that occurs as the size of MOSFET is reduced. The short-channel effect introduces several leakage current mechanisms in MOSFET such as reverse-bias p-n junction current, weak inversion current, and drain induced barrier lowering (DIBL) current.

Another effect that occurs as the MOSFET is scaled down is tunneling effect. Normally, the transistors are separated sufficiently enough so that the operation of one transistor does not affect another transistors. The separation is made by inserting material that acts as a barrier between any two transistors. However, as the size of MOSFET is made very small and the barrier distance is also small, there is possibility that the carriers of one MOSFET cross the barrier. The tunnelling effect increases exponentially as the barrier distance is decreased.

Another limitation to MOSFET scaling is the fact that the threshold voltage does not decrease at the rate proportional to channel length. Threshold voltage is defined as the gate voltage at which current starts to flow in the channel.

All these factors affect the process of scaling MOSFET further down too deep in nanoscale range. Hence, it is necessary to find solution by introducing new type of device that can replace MOSFET in near future that will not only continue what MOSFET can do today but also can support high demand in future applications.

One of the promising nanoelectronic devices for nanotechnology era is carbon nanotube field-effect transistor (CNTFET). The structure of CNFET is almost the same as MOSFET but the silicon channel is replaced by semiconducting carbon nanotube. The schematic diagram of CNTFET structure is shown in Figure 8 [21].
2.2 Carbon Nanotubes

Carbon nanotubes (CNTs) are allotropes of carbon and members of the fullerene structural family, which also includes buckyballs. Whereas buckyballs are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. The diameter of a nanotube is on the order of a few nanometers, while they can be up to several millimeters in length. There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

A single wall carbon nanotube is a one-atom thick sheet of graphite (called graphene) rolled up into a cylinder along an \((a_1, a_2)\) lattice vector in the graphene plane (Figure 9). The \((a_1, a_2)\) indices determine the diameter and chirality, which are key parameters of a nanotube. Depending on the chirality, SWNTs can have either metallic or semiconducting properties [22].
The nature of the bonding in a nanotube is described by quantum chemistry, specifically, orbital hybridization. The chemical bonding of nanotubes are composed of sp2 bonds, similar to those of graphite. This bonding structure, which is stronger than the sp3 bonds found in diamond, provides the molecules with their unique strength. Nanotubes naturally align themselves into ropes held together by Van der Waals forces [23].

2.2.1 Discovery of Carbon Nanotubes

Most of literature attributes the discovery of carbon nanotube to Iijima of NEC in 1991 [6]. Monthioux and Kuznetsov [24] described the interesting and often misstated origin of this nanostructure. Carbon nanotubes have been synthesized and observed prior to 1991. In 1976, Oberlin, et al. [25] observed hollow carbon fibers with nanometer-scale diameters. The authors also show a TEM image of a nanotube consisting of a single wall of graphene. Later, Endo has referred to this image as a single-walled nanotube.
Carbon nanotube research accelerated greatly following Iijima’s discovery of single-walled carbon nanotubes and methods to specifically produce them by adding transition-metal catalysts to the carbon in an arc discharge [26].

2.2.2 Physical Properties of Carbon Nanotubes

Due to the covalent sp² bonds formed between the individual carbon atoms, carbon nanotubes are the strongest materials in terms of tensile strength. Multi-walled carbon nanotubes have a tensile strength of 63 GPa. Since carbon nanotubes have a low density for a solid (1.3-1.4 g·cm⁻³) its specific strength of up to 48,000 kN·m·kg⁻¹ is the best of known materials, compared to high-carbon steel's 154 kN·m·kg⁻¹ [27].

Under excessive tensile strain, carbon nanotubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5% and can increase the maximum strain. The tube undergoes before fracture by releasing strain energy.

CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsional or bending stress.

2.2.3 Electrical Properties of Carbon Nanotubes

The electrical properties of carbon nanotubes (CNT) are unique. Unlike most materials, they come in both metallic and semiconducting forms, based on the chirality (Figure 10) [28]. There are three types of carbon nanotubes based on their chirality:
zigzag, armchair, and chiral. Those three types of chirality are determined by the angle of how the graphene sheet is rolled. This is shown in Figure 11 [29].

Figure 10: Three types of chirality in carbon nanotubes [29]
Figure 11: Metallic or semiconducting properties of carbon nanotubes, depending on which point the (0, 0) point is rolled to.

Armchair carbon nanotubes will always have metallic properties, while the others can be metallic or semiconductor. If the (0, 0) point is folded to any of the points along the armchair line, we get a metallic nanotube. However if it is folded along the zigzag line or in the chair area, which is the area between the zigzag and armchair, we get either semiconductor or metallic tube.

2.2.4 Ballistic Transport in Carbon Nanotubes

Ballistic transport occurs when the mean free path is larger than the length the carrier travels. The mean free path is the average length that a carrier has to travel before it encounters a scattering event. The carrier can be scattered by many different sources,
such as both acoustic and optical phonons that are vibrations in the lattice, ionized impurities, defect, interfaces, and even other carriers.

The mean free path is inversely proportional to the temperature, so the lower temperature nanotubes have longer paths. We compare this to metals, such as copper, whose mean free paths are approximately on the order of tens of nanometers. This is because of a reduction in the cross-section of a scattering event due to the 1-D nature of the nanotube. At room temperature, acoustic phonons do not possess enough momentum to change the carrier’s direction. So unlike metals, where a carrier can use multiple small angle scattering events to reverse its direction, the 1-D nanotube forces carriers to move only back and forth eliminating the possibility of small angle scattering events reversing the electrons direction. While optical phonons have enough momentum to reverse the direction of carriers, they are too energetic to exist at room temperature and at low voltages.

Due to the ballistic conductance and the strong covalent bonds between the carbon atoms, the nanotube is able to achieve current densities of \(2.5 \times 10^9\) A/cm\(^2\). This is significantly higher than any type of interconnect used in today’s circuits.

### 2.2.5 Multi-walled Carbon Nanotubes (MWCNTs)

MWCNTs are composed of multiple concentric SWNT shells (Figure 12) [30]. Their properties are complicated, since each SWNT shell has different properties from the other shells. However, it has been discovered that the outer shell contributes most of the electrical properties of a MWCNT.
MWCNTs were first reported by Ijima in 1991. The space between the cylindrical layers of graphite corresponds to the d-spacing of graphite (0.345 nm). The inner diameter of multiwall nanotubes ranges between 3 to 20 nm and the outer diameter is defined by the number of layers. MWCNTs are typically formed with the DC carbon arc or laser vaporization method. The carbon source is usually a graphite rod that will be evaporated either by an electrical spark or a laser pulse. When the vapors of carbon condense, multiwall nanotubes are formed as well as amorphous carbon. The temperature used for their synthesis is different depending on the process. Direct current (DC) carbon arcs can reach locally temperatures as high as 3273 K while laser vaporization is done at 1473 K [31]. Chemical vapor deposition (CVD) can also be used to synthesize multiwall nanotubes. The temperature of reaction is typically between 1073 K and 1473 K, and the gas source is usually methane, carbon monoxide or ethylene. The growth promoter is nearly always either a pure transition metal such as iron, nickel or cobalt or an alloy based on one or more of those metals.
2.3 Fabrication and Performance of CNT-based Transistors

The first carbon nanotube field-effect transistors (CNTFETs) were fabricated in 1998 [32, 33]. A single SWCNT was used to bridge two noble metal electrodes prefabricated by lithography on an oxidized silicon wafer as shown in Figure 13 [33].

![AFM image of one of our early CNTFETs. Schematic cross section of the CNTFET](image)

**Figure 13:** Top: AFM image of one of our early CNTFETs. Bottom: Schematic cross section of the CNTFET [19]

The SWCNT played the role of the “channel”, while the two gold electrodes functioned as the source and drain electrodes. The heavily doped silicon wafer itself was used as the “gate” (back-gate). These CNTFETs behaved as p-type FETs and had an \( I_{\text{on}}/I_{\text{off}} \) current ratio of \( \sim 10^5 \).

Carbon nanotube was simply laid on the gold electrodes and was held by weak Van der Waals forces. To improve the contacts, Martel et al. adapted a different fabrication scheme where the semiconducting SWCNTs (s-
SWCNTs) were dispersed on an oxidized Si wafer, and the source and drain electrodes, now made of metals that are compatible with silicon technology such as Ti or Co, were fabricated on top of them. Thermal annealing of the contacts, which in the case of Ti electrodes led to the formation of TiC, produced a stronger coupling between the metal and the nanotube and a reduction of the contact resistance [Error! Bookmark not defined.,34].

Figure 14 shows the output and transfer characteristics of such a CNTFET with Co electrodes. The transistor is p-type and has a high on–off current ratio of $\sim 10^6$. This new CNTFET configuration has a significantly reduced contact resistance, $\sim 30 \, \text{k}\Omega$, and a transconductance $g_m = 0.34 \, \mu\text{S}$, $\sim 200$ times higher than that of van der Waals-bonded CNTFETs [34].
Figure 14: (a) Output characteristics of a CNTFET with cobalt source and drain electrodes deposited on top of tube. (b) The corresponding transfer characteristics

The early CNTFETs were back-gated with very thick gate insulators (SiO$_2$ thickness: ~ 100-150 nm). By reducing the insulator thickness or increasing the dielectric constant, the gate capacitance could be increased. A next generation of CNTFETs with top gates was fabricated by dispersing SWCNTs on an oxidized wafer. Atomic force microscopy (AFM) imaging was used to identify single CNTs, and the Ti source and drain electrodes were fabricated on top of by e-beam lithography and liftoff [35]. After
annealing at 850 °C to transform the contacts into TiC, a 15- to 20-nm-gate dielectric film was deposited by chemical vapor deposition (CVD) from a mixture of SiH₄ and O₂ at 300 °C. After annealing for ~0.5 h at 600 °C in N₂ to densify the oxide, 50-nm-thick Ti or Al gate electrodes were patterned by lithography and liftoff.

Figure 15 shows a schematic of a top-gated CNTFET, and the output characteristics of such a device with Ti electrodes and a 15 nm SiO₂ gate insulator film. This CNTFET can also be switched by the bottom gate (wafer) and the resulting characteristics can be compared with those of the device under top-gate operation. This device has a superior performance; the threshold voltage of the top-gated CNTFET is significantly lower, -0.5 V, than under bottom-gated operation, -12 V. Similarly, the drive current is much higher under top gating, and the transconductance is similarly high, \( g_m = 3.3 \ \mu\text{S} \) per nanotube.
Figure 15: (a) Schematic representation of one of our top-gated CNTFET with Ti source, drain, and gate electrodes. (b) The I–V characteristics of the device [35]

Table 1 shows the comparison of the characteristics of the CNTFET with two recent high-performance Si p-channel devices: a 15-nm-gate length MOSFET built on bulk silicon – Ref A [36] and a 50-nm-gate length device built using SOI technology – Ref B [37].
Table 1: Comparison of Key Performance Parameters for a 260 nm-Long Top Gate p-CNTFET, a 15-nm-Bulk Si p-MOSFET (Ref. A), and a 50-nm SOI p-MOSFET (Ref. B) [36, 37]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>p-type CNTFET</th>
<th>Ref a</th>
<th>Ref. b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gate Length (nm)</td>
<td>260</td>
<td>15</td>
<td>50</td>
</tr>
<tr>
<td>Gate oxide thickness (nm)</td>
<td>15</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>$V_t$ (V)</td>
<td>-0.5</td>
<td>~-0.1</td>
<td>~-0.2</td>
</tr>
<tr>
<td>$I_{ON}$ (μA/μm)</td>
<td>2,100</td>
<td>265</td>
<td>650</td>
</tr>
<tr>
<td>($V_{DS} = V_{GS} - V_t \sim -1$ V)</td>
<td>-150</td>
<td>&lt;500</td>
<td>-9</td>
</tr>
<tr>
<td>$I_{OFF}$ (nA/μm)</td>
<td>130</td>
<td>~100</td>
<td>70</td>
</tr>
<tr>
<td>Subthreshold slope (mV/dec)</td>
<td>2,321</td>
<td>975</td>
<td>650</td>
</tr>
<tr>
<td>Transconductance (μS/μm)</td>
<td>2,321</td>
<td>975</td>
<td>650</td>
</tr>
</tbody>
</table>

It can be seen that the CNTFET is capable of delivering three to four times higher drive currents than the Si MOSFETs at an overdrive of 1 V, and has about four times higher transconductance. From the above and other considerations, it is clear that CNTFETs can be very competitive with the corresponding Si devices.

2.4 Multiwalled Carbon Nanotube Field-Effect Transistors

The discussion above has been limited to transistors made out of single-walled carbon nanotubes (SWCNTs). In MWCNTs side-bonded to metal electrodes, effectively only the outer shell contributes to electrical transport [38]. MWCNTs with a semiconducting outer shell could be used to fabricate CNTFETs. However, in semiconducting CNTs, the band gap is inversely proportional to the tube diameter. Therefore, only small-diameter MWCNTs are expected to display large switching ratios at room temperature.
Figure 16 shows the effect of the gate voltage on the conductance (G) of a 14-nm diameter MWCNT measured at different temperatures. The gate can modulate the conductance of the MWCNT channel at room temperature. However, there is a large residual conductance, which can be assigned to the coupling of the outer semiconducting shell to an inner metallic shell. This coupling is expected to be activated with an activation energy on the order of $\sim E_{\text{gap}} / 2$. At low temperatures, the contribution of the inner metallic shell is suppressed. These observations indicate that the transport characteristics of an MWCNT at ambient temperature may have contributions from more than the outer shell even for side-bonded CNTs. Because of the activated nature of the shell-to-shell transport, and given that the semiconducting gap is inversely proportional to the CNT diameter, multishell transport should be more important for large-diameter tubes [38].

![Graph showing temperature dependence of conductance](image)

**Figure 16**: Temperature dependence of the conductance $G$ of an MWCNT as a function of the gate voltage
2.5 Carbon Nanotubes for Electrical Interconnect Applications

Carbon nanotubes have been investigated as candidate materials to replace or augment the existing copper-based technologies for on-chip interconnects. The basis for these studies is a derivative of their robust thermal [39], electrical [40], and mechanical [41] properties, in addition to their high-aspect ratio.

The need to find alternative interconnect materials is imperative as copper resistivity is rapidly increasing with decreasing linewidth, inevitably causing latency issues due to both line resistance [Error! Bookmark not defined.,Error! Bookmark not defined.] and load capacitance [42]. The most troublesome issue with the current state-of-the-art copper interconnects is the reliability concern due to electromigration [42]. Initial electrical characterization results, using carbon-based nanostructures for interconnect applications, have been demonstrated [43,44,45], providing encouraging trends for their implementation in next generation circuit integration schemes.

2.6 Comparison between Carbon Nanotubes and Copper Nanowires as Interconnects

To better understand and more precisely measure the key characteristics of both copper nanowires and carbon nanotube bundles, the researchers at Rensselaer Polytechnic Institute used advanced quantum-mechanical computer modeling to run vast simulations on a high-powered supercomputer. It is the first such study to examine copper nanowire using quantum mechanics rather than empirical laws.

With the help of Rensselaer's Computational Center for Nanotechnology Innovations, the research team concluded that the carbon nanotube bundles exhibited a
much smaller electrical resistance than the copper nanowires. This lower resistance suggests carbon nanotube bundles would therefore be better suited for interconnect applications.

With this study, the researchers have provided a road map for accurately comparing the performance of copper wire and carbon nanotube wire. Carbon nanotubes at 45 nanometers will outperform copper nanowire. Because of the nanoscale size of interconnects, they are subject to quantum phenomena that are not apparent and not visible at the macroscale. Empirical and semi-classical laws cannot account for such phenomena that take place on the atomic and subatomic level, and, as a result, models and simulations based on those models cannot be used to accurately predict the behavior and performance of copper nanowire. Using quantum mechanics, which deals with physics at the atomic level, is more difficult but allows for a fuller, more accurate model.

The size of computer chips has shrunk dramatically over the past decade, but has recently hit a bottleneck. Interconnects, the tiny copper wires that transport electricity and information around the chip and to other chips, have also shrunk. As interconnects get smaller, the copper's resistance increases and its ability to conduct electricity degrades. This means fewer electrons are able to pass through the copper successfully, and any lingering electrons are expressed as heat. This heat can have negative effects on both a computer chip's speed and performance.

Researchers in both industry and academia are looking for alternative materials to replace copper as interconnects. Carbon nanotube bundles are a popular possible successor to copper because of the material's excellent conductivity and mechanical integrity. It is generally accepted that a quality replacement for copper must be
discovered and perfected in the next five to 10 years in order to further perpetuate Moore's Law that states the number of transistors on a computer chip, and thus the chip's speed, should double every 18-24 months.

There are still many challenges to overcome before mass-produced carbon nanotube interconnects can be realized. There are still issues concerning the cost of efficiency of creating bulk carbon nanotubes, and growing nanotubes that are solely metallic rather than their current state being of partially metallic and partially semiconductor. More study will also be required to study the carbon nanotubes and the characteristics of carbon nanotube interconnect.

2.7 Fabrication of Carbon Nanotube-based Interconnects in situ via Chemical Vapor Deposition

Carbon nanotubes can be produced by using arc discharges, laser ablation of a carbon target, or chemical vapor deposition (CVD). In all of these techniques, a metal catalyst (typically Co, Fe, and/or Ni) in the form of nanoparticles is utilized.

CNT-based electronic devices were fabricated by random deposition of CNTs on a pre-patterned substrate (direct random approach) or the pattern of metallic contacts onto randomly deposited CNTs after their observation (indirect random approach). Langer and coworkers first reported electrical resistance measurements on individual MWCNT [46]

Carbon nanotube field-effect transistors (CNTFETs) introduced by IBM in 1998 were made by dispersing carbon nanotubes (produced by laser ablation or arc-discharge evaporation) by sonication in a dichloroethane solution and then spreading them on a
substrate with predefined electrodes [47]. While this technique demonstrated the feasibility of CNTFETs, the processing limited the number of transistors per chip, as not all nanotubes spread on the substrate will fall exactly on the desired sites. Therefore, a novel processing technique is needed to efficiently and effectively produce commercial CNTFETs.

Currently, catalytic CVD is the most widely used technique to grow carbon nanotubes. One of the advantages of this approach is that it allows nanotubes to be grown locally by placing the catalyst at the appropriate location. Controlled parallel growth of CNTFETs in-situ via chemical vapor deposition is a way to solve the processing difficulties to make many CNTFETs at once.

Bazzana et al. [48] have demonstrated the ability to grow carbon nanotubes by chemical vapor deposition using CO, CH₄, CO₂, H₂, and H₂O as the reactant gases. Nickel nanoparticles, used as catalysts for CNT growth, were made by evaporating nickel onto the substrate and heating at 1173K under 20 sccm flowing hydrogen to make catalyst islands.

2.8 Comparison between Various Fabrication Methods of Carbon Nanotube-based Electrical Interconnects in The Literature

There are several methods of fabricating carbon nanotube-based electrical interconnects found in the literature. Fujitsu [45,49] grown carbon nanotubes using hot-filament catalytic chemical vapor deposition (HF-CCVD) and Co/Ti bilayer films. The CNTs were grown from Co particles in acetylene (C₂H₂) at 1000 Pa and 540°C for 10
min. Vertically aligned CNTs were observed on Co (2.5 nm)/Ti (2.5 nm) bilayer films by scanning electron microscopy (SEM). CNTs were grown over the entire surface of a 200 mm-diameter Si wafer using Co (1.0 nm)/Ti (1.0 nm) bilayer film. For the electrodes, a 2.5-nm-thick Ti film was deposited by rf magnetron sputtering and patterned by Ar ion milling. The electrical properties of the CNT interconnects were evaluated by the two-terminal method, showing the resistance of 0.59 Ω.

Ngo, et al. [50] grew vertically aligned, freestanding carbon nanofiber arrays by plasma-enhanced chemical vapor deposition (PECVD) from a 35 nm thin film of Ni on a 30 nm Ti electrode deposited on silicon. For Pd-catalyzed nanofibers, a 20 nm thin film is used on a 30 nm Ti electrode deposited on silicon. The top contact pad was made by depositing Ti/Pt on top of the vertical carbon nanofiber arrays.

The room-temperature measurements were performed using a wafer probe station with a two-terminal configuration. This electrical characterization revealed the resistance values of 13.3 kΩ for Ni-catalyzed interconnects and 9.0 kΩ for Pd-catalyzed interconnects. These resistance values are higher compared to Fujitsu’s (0.59 Ω), Samsung’s (1.2 kΩ) [51], and Infineon’s (7.8 kΩ) [52]. Therefore, this fabrication method resulted in electrical interconnect with high resistance. Furthermore, there was only one pair of electrodes per chip, which means that there were still many challenges to fabricate mass-produced carbon nanotube interconnects.

In summary, there are several methods to fabricate carbon nanotube-based interconnects found in the literature. However, the main limitation is those fabrication methods is the difficulty to fabricate multiple electrical interconnects per chip. Therefore,
another method to fabricate multiple interconnects per chip at once needs to be investigated.
3.0 EXPERIMENTAL

In order to study the fabrication methods to build the carbon nanotube field interconnects, there are three main experimental steps. The first step is to investigate the nanopatterning technique used for controlling the sites and directionality of carbon nanotube growth. The second step is to investigate the in-situ carbon nanotube growth between pre-patterned gold electrodes. Finally, the third step is to characterize the resulting carbon nanotube interconnects.

3.1 Investigation of The Nanopatterning Technique to be Used for Controlling The Sites and Directionality of Carbon Nanotube Growth

To investigate the nanopatterning technique for controlling the sites and directionality of carbon nanotube growth, first of all, a design of nanopatterns on a substrate was made. Figure 17 and Figure 18 show the schematic diagram of the nanopatterns, consisting of gold electrodes and troughs. Those electrodes and troughs are on a silicon (Si) substrate with SiO₂ layer on top. With this pattern, carbon nanotube networks will only be grown in specific locations, i.e., along the troughs / between a pair of gold electrodes. Furthermore, with the narrow troughs, the cross sectional area of carbon nanotube networks can be minimized, which is better for interconnects. However, because of some issues regarding e-beam lithography (will be described later), the troughs could not be made.
Figure 17: Schematic Diagram of CNT Network Sites

Figure 18: Schematic Diagram of Pattern for Interconnects
All nanopatterning procedures were performed at the Kostas Facility for Micro and Nanofabrication at Northeastern University. First, the silicon substrate was cleaned by using the standard pre-diffusion cleaning procedure:

1. Piranha Etch: 10 minutes, to remove organics and metals
   
   (2 vol. of H₂SO₄ : 1 vol. of H₂O₂ at 105-115°C)

2. Cascade Rinse: 5 minutes

3. Native thin film oxide removal with 50:1 HF (50 of H₂O : 1 of 49% HF) for 15 s

4. Cascade Rinse: 5 minutes

5. 10 minutes H₂O:HCl:H₂O₂ (6:1:1, vol, at 95°C) rinse to remove remaining metallic impurities

6. Cascade Rinse: 5 minutes

7. Rinser dryer for 7.5 minutes (150 s rinser, 300 s dryer).

Figure 19 shows the vented wet bench and dump rinser to perform those cleaning procedures [53].
After cleaning, silicon wafers were placed into a high temperature furnace (900°C < T < 1200°C) in the presence of oxygen or water where the following reaction occurs:

\[
\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2
\]

or

\[
\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + \text{H}_2
\]

By controlling temperature and oxidation time precisely, oxide thickness can be predicted and controlled accurately [54]. Figure 20 shows the furnace in Kostas Center used to grow SiO₂ layer on top of Si [53].
The thickness of SiO$_2$ formed on silicon substrate was measured with Nano-Spec Optical Profilometer (Figure 21). This equipment is used for non-contact film thickness determination by using white light optical spectrometer. After oxide growth, Si/SiO$_2$ was then diced into 1.5 cm $\times$ 1.5 cm chips (Figure 22).
After wafer preparation, the next step is to do nanoscale patterning by using electron beam (e-beam) lithography. Electron beam lithography is the practice of scanning a beam of electrons in a patterned fashion across a surface covered with a film (called the resist), and of selectively removing either exposed or non-exposed regions of the resist. The purpose is to create very small structures in the resist that can subsequently...
be transferred into another material for a number of purposes, for example for the creation of very small electronic devices.

The primary advantage of electron beam lithography is that it is one of the ways to beat the diffraction limit of light and make features in the nanometer regime. This form of maskless lithography has found wide usage in mask-making used in photolithography, low-volume production of semiconductor components, and research & development. This e-beam lithography technique will be investigated as a feasible way to grow carbon nanotube networks in specific locations with narrow width (to make the cross-sectional area of carbon nanotube network smaller).

First, Si/SiO$_2$ was spin coated with 2 types of PMMA (polymethylmethacrylate): 495K A2 and 950K A2 (Figure 23) by using Brewer 100 CB PhotoResist Spinner (Figure 24). Then, “soft bake” was performed with these steps:

- Spin coat PMMA 495K A2 (90 s at 5000 rpms – thickness ~50 nm)
- Bake on hotplate at 180 °C for 90 s
- Spin coat PMMA 950K A2 (90 s at 5000 rpms – thickness ~60 nm)
- Bake on hotplate at 180 °C for 90 s
- After the baking process, Si/SiO$_2$ with PMMA on top was ready for e-beam patterning.

In Kostas Center, e-beam lithography was performed by using SEM Zeiss Supra 25. This SEM contains the J.C. Nabity version 9 software for e-beam lithography and pattern generation system.
After e-beam patterning, the development of the sample was performed to remove exposed PMMA. This process consists of three steps:
• 70 s development in mixture of MIBK (methyl isobutyl ketone) & IPA (isopropyl alcohol)
• Volumetric ratio of MIBK:IPA = 1:3 (vol)
• 30 s rinse in IPA
• ≥ 30 s final rinse in deionized water

Both area dose and line dose e-beam lithography were performed (Figure 25). With line dose, smaller width of trough was able to be patterned. Another way to reach smaller width of trough was by using ‘hard bake’ (instead of ‘soft bake’). The procedure for hard bake is:

• Spin coat PMMA 495K A2 (90 s at 5000 rpms – thickness ~50 nm)
• Bake on hotplate at 180 °C for 90 s
• Spin coat PMMA 950K A2 (90 s at 5000 rpms – thickness ~60 nm)
• Bake on hotplate at 180 °C for (90 s + 30 min)
3.2 Investigation of In-situ Carbon Nanotube Growth between Pre-patterned Gold Electrodes

To investigate the nanopatterning technique for controlling the sites and directionality of carbon nanotube growth, first, gold electrodes were patterned on Si/SiO₂ substrate. After that, nickel thin film was deposited on specific sites via thermal evaporation. The sample was then placed in a thermogravimetric reactor for annealing of Ni thin film and growth of carbon nanotube networks.

3.2.1 Patterning of Gold Electrodes

Pairs of gold electrodes with certain dimensions (Figure 26) were patterned by photolithography and evaporation. This was done by Onnaz Ozkanat at the Harvard’s Center for Nanoscale Systems (CNS). The aperture width (l) was 30 µm.
3.2.2 Placement of Nickel Nanoparticles

To grow carbon nanotubes at specific sites, nickel nanoparticles, which act as the catalyst of carbon nanotube growth, have to be placed at those specific sites as well (Figure 27).

Because of the issues regarding e-beam lithography’s post development process, micromasking procedures (line pattern and circle pattern) were developed (Figure 28 and Figure 29). The purpose of micromasking, similar to e-beam lithography, is to place
nickel thin film at specific sites. Even though the area of Ni thin film deposition via micromasking is larger than that of e-beam lithography, this micromasking technique has an advantage: the mask is easy to remove after Ni deposition, while there are some problems in removing photoresists used in e-beam lithography. Another advantage of micromasking is related to the position of the hole. The hole/opening of the mask needs to be positioned on the correct sites, i.e., between a pair of gold electrodes. With e-beam lithography, it is extremely hard to exactly position this hole on the desired sites, as the aperture between a gold electrode pair cannot be seen after the substrate is covered by photoresist (PMMA). With this micromasking technique, the hole can be placed exactly on top of the aperture, with the aid of optical microscope.

For circle pattern, aluminum foil and transparent film/plastic were used as the masks. It was found out that the transparent plastic was better that aluminum foil as the micromasking material. The mask’s hole could be easily placed on top of the gold electrodes’ aperture (Figure 30 and Figure 31).

**Figure 28: Schematic Diagram of Line Pattern**
Figure 29: Schematic Diagram of Circle Pattern

Figure 30: Schematic diagram of “micromasking” using Al foil
3.2.3 Thermal Evaporation for Nickel Thin Film Deposition

A Denton Vacuum DC Magnetron sputter system (DV 502A) equipped with optional thermal-evaporation was used for the thin film deposition. Two metals could be coated by plasma magnetron: chromium (UHP) and gold (UHP). The advantage of the plasma magnetron technique is the ability to control the thickness of the thin film deposited and the multi-directional coating (no shadow effect). Thin films in the order of 1-2 nm could easily be obtained. Before depositing the thin film, the chamber was evacuated to $2 \times 10^{-7}$ torr and then the plasma was ignited under a pressure of $5 \times 10^{-3}$ torr of research grade argon. However, not every metal can be sputtered. To make thin film of other metals such as nickel, iron or cobalt, thermal evaporation was used. The sample was placed 20 cm below a new tungsten basket in which metal to evaporate was placed.
The chamber was evacuated to $9 \times 10^{-7}$ torr and the metal was evaporated when 10-12 amps were provided across the tungsten basket (Figure 32) [55].

Figure 32: Denton Nickel Evaporation Chamber

3.2.4 Reactor System for Annealing of Nickel Thin Film and Carbon Nanotube Growth

A precise feed gas delivery system, which could be operated manually or automatically, was used to deliver accurate mixture of gases to the reactor (Figure 33). An online gas chromatograph was used to verify the composition of the reactant gases and product gases during reaction.
The experimental apparatus was composed of three subsections (Figure 34). The first section was the feed-gas delivery system in which the inlet gases were metered (manually or digitally), mixed and delivered either dried or saturated with water. The second section was two identical thermogravimetric reactors composed of a catalyst assembly within a quartz reactor tube. The third section was a data acquisition subsystem. Each valve used to direct a gas feed stream was a solenoid valve controlled by a switch. All the lines used to connect each part of the system were either stainless steel grade 316 (Outside Diameter of $6.35 \times 10^{-3}$ m) or flexible Teflon lines inside a stainless steel grade 316 overbraid. All fittings were Swagelok® fittings made of stainless steel grade 316.
3.2.4.1 Feed-gas Delivery

Seven gases were used during this investigation. Helium and argon were used for safety, dilution and cooling purposes. Methane, carbon dioxide, carbon monoxide, water and hydrogen were used as reactant gases. All gases were purchased from Medtech. A typical analysis of each gas is given in Table 2. Prior to entering the experimental apparatus, carbon monoxide was sent through a “carbonyl destruction chamber” composed of a quartz tube packed with quartz wool and heated at 625 K. The purpose of this chamber is to decompose any iron carbonyl that may have been present in the gas. The gases could be individually fed to either reactor in one of two different ways. If the experiment was to be conducted manually, gases were fed to Brooks Model 8944 mass flow regulators. Each outlet of the 8944 mass flow regulators was directly connected to a precision bore
capillary tube (ID 1 mm and 0.90 m in length) in combination with a manometer containing Meriam high vacuum manometer fluid (specific gravity 1.04).

<table>
<thead>
<tr>
<th>Gas Grade</th>
<th>Purity %</th>
<th>Impurities ppm</th>
<th>N₂</th>
<th>O₂</th>
<th>CO &amp; CO₂</th>
<th>THC</th>
<th>H₂O</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>U.H.P.</td>
<td>99.999</td>
<td>10.5</td>
<td>7</td>
<td>2</td>
<td>-</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>CO</td>
<td>U.H.P.</td>
<td>99.97</td>
<td>63</td>
<td>20</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>CH₄</td>
<td>U.H.P.</td>
<td>99.99</td>
<td>101</td>
<td>60</td>
<td>10</td>
<td>4</td>
<td>3</td>
<td>C₂H₆:20</td>
</tr>
<tr>
<td>CO₂</td>
<td>U.H.P.</td>
<td>99.99</td>
<td>11</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>0.05</td>
<td>1</td>
</tr>
<tr>
<td>He</td>
<td>U.H.P.</td>
<td>99.999</td>
<td>19.5</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>Ar</td>
<td>U.H.P.</td>
<td>99.999</td>
<td>10.5</td>
<td>-</td>
<td>3</td>
<td>2</td>
<td>0.5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2: Purity of the reactant gases used

The ends of the capillary tubes were flared to reduce the perturbations, created during the gas stream transition from the 6.35 mm OD line into the capillary tube. A trap was placed at the outlet of the manometer to prevent an accidental overflow of Meriam fluid into the system. These manometers were used to obtain calibration curves of flow rate in cm³/s (NTP) versus pressure drop in centimeters of Meriam fluid for each reactant gas. These calibration curves were then corrected for Standard Temperature and Pressure (i.e., T=273.15 K and P=1 atm), and could be used to establish the desired gas phase composition. If the experiment was to be conducted digitally, gases were fed to Brooks model 5850E digital mass flow controllers with Brooks model 0154E external display.
with an accuracy of ±0.3 cc/s. The manual mass flow controllers were used to calibrate the digital mass flow controllers. Once the manual and digital mass flow controllers were calibrated, they could be used separately to set up two different compositions at the same time.

A total of three independent feed-gas delivery systems were built: two manual and one digital. A digital system and one of the manual systems could be used to deliver reactants, the other manual system was used for conditioning and testing purposes. Independently of the method used to set up the gas phase composition, gases were mixed and dried in a 304L-HDF 316 stainless steel cylinder (300 cm³) filled 1/3 with 5A molecular sieves and 2/3 with Drierite®. Then mixed gases were either fed to the reactor or vented to atmosphere (used to set up changes in reaction's conditions). When the gases were fed to the reactor they could be either fed dry or saturated with water. Two identical saturators were built. One was for the gases coming out from the digital mass flow controller lines, and the other for the gas mixture coming out from the manual mass flow controller feed-line. An ensemble of three ways solenoid valves could alternate the saturators from one line to the other or placed the saturators in series.

3.2.4.2 Water Saturator

Figure 35 illustrates the components for the saturator system. Only three of the five Kimax flasks used have been represented. The feed gases were fed through a 6.35 mm OD preheated copper line. Insulated heating tapes of 209 Watt from Thermolyne were used to heat the lines up to 381 K. A 600 Watt variac controlled the power for the heating tapes. The gases proceeded through Kimax flasks of 500 mL that were connected
in series and submerged in a 40 liters glass container. A heating coil/mixer (750 Watt) from Fisher was used to heat the water bath. The temperature was controlled by an Omega CN9000A controller to ± 0.1ºK of set point. The temperature of the bath was monitored by a Omega chrome-alumel K thermocouple. The bath circulation was provided by an electric motor-propeller assembly with variable speed. The walls of the water bath were insulated with fiber glass to reduce heat losses. The gas stream was fed to each flask through Kimax fritted glass gas-dispersion tubes, and was passed from flasks to flasks with an 3/8” OD Tygon tubing which was also submerged. After the fourth flask, the saturated gases were fed through a fifth Kimax 0.5 L flask filled with 0.5 mm diameter glass beads and then through 3 cm of glass wool. This was necessary to prevent small droplets from being entrained with the saturated gas stream. A thermocouple Chrome-alumel K type was present in the last flask to record the temperature of the saturated gases and hence calculate the amount of water added to the gases. The partial pressure of water vapor to be used in an experiment was set equal to the equilibrium vapor pressure at the bath’s temperature. The saturated feed gas stream then entered the reactor through heated feed lines. These lines were heated above 373 K using 209 Watt heating tapes from Thermolyne. Each heating tape was controlled by a 600 Watt variac.
If the gases were to be fed dry, after passing through the mixing devices, another combination of three way solenoid valves would send the dry gases directly to the reactors, bypassing the saturator lines. Finally another combination of solenoid three way valves would have the ability to send the reactant gas stream to one reactor or the other.

3.2.4.3 Reactor

The reactor tube (Figure 36) was composed of two sections: a heated quartz reactor tube and a cooler extension made from Pyrex. The cooler extension served to connect the hot reactor tube (900 K) to the electronic balance chamber at room temperature (298 K). The quartz section of the reactor was ~ 0.038 m in diameter and 0.66 m in length. The reactor tube and the extension were mounted vertically. The bottom
of the reactor was tapered, and with a Vycor fitting directly connected to a 316 stainless steel Swagelok union tee. The reactor tube was partially filled with quartz Rashig rings 0.8 cm length and 0.8 cm diameter, up to a height of 0.24 m from the bottom. These rings provided a preheating zone for the reaction gases. A temperature profile of the reactor is presented in Appendix B. The isothermal zone (±1ºK) started 2.5 cm above the packing and had a length of 2 to 3 cm. The temperatures of the reactor were monitored by chrome-alumel (type K) thermocouples from Omega. The thermocouples were passed through the stainless steel union tee at the bottom of the reactors and through the packing, up to the isothermal zone.
Figure 36: Reactor tube, all dimensions are in centimeters [56]
To avoid direct contact between thermocouples and the reactant gases, thermocouples were placed inside an aluminium oxide, non permeable tube, Omegatite 450 from Omega. The heat for each reactor was supplied by two identical furnaces, ATS 3210. These furnaces were composed of two independent zones of heating elements which could achieve temperatures as high as 1373 K. Each zone of each furnace was controlled by a Eurotherm controller programmer Type 2404. These controllers could be used to linearly increase the temperature of the reactor, ensuring reproducible heating of individual samples.

All samples were suspended from the balance into the reactor by a Nichrome hang down wire and a thin fused quartz rod in series. The first wire was an extension wire from the arm of the balance to the end of the Pyrex extension tube. The second part of the hang down assembly was a fused quartz rod. Fused quartz was used to avoid any unwanted reaction in the reactor near the sample. The total length of the wires was such that the sample was suspended in the isothermal zone when the reactor was in the closed position. A 6 mm O.D. quartz tube was positioned in close proximity to the sample for gases analyses. The Pyrex extension tube increased the distance between the reactor at 900 K and the balance chamber at 298 K. This Pyrex extension tube was 3.8 cm in diameter and 23 cm in length. A restriction was made 14.5 cm from the top of the Pyrex tube. This restriction had an orifice of 0.95 cm in diameter. Just above the orifice a vent port was located. A second vent port was located under the orifice and extended to 27 cm down in the quartz reactor tube. Inert gas, such as helium, was sent in the balance chamber at a flow rate of 40 cm$^3$/s (STP) and down the Pyrex extension tube to the orifice. A portion of this stream was vented through the first vented port. The remaining
gas went through the orifice, preventing reactant gases from entering the balance chamber. The inert gas would then mix with the reactant gases inside the reactor and above the sample before going through the second vent port. Both complete reactor systems (balance chamber, extension Pyrex tube, quartz reactor and furnace) were mounted on vibration frames. These frames were each supported by three pneumatic pistons from Vibraplane. Each piston was under a pressure of 276 Kpa (40 Psi). This frame was used to ensure a maximum sensibility for the balance ($10^{-7}$ g). In order to align the centers of gravity of both the frame and the reactor system and to damp vibrations, additional weights were distributed between the pistons (50 kg) on the frame. All connections to the reactors (inlet and outlet of the reactor, power lines for the furnace and data cables for the Cahn balance) were passed through sand bags to damp additional vibration pathways.

### 3.2.5 Manual or Automatic Controllers

Each valve used in the system was a solenoid valve red hat II, purchased from Asco. The valves were either 2 way normally open, 2 way normally closed or 3 way universal. Each valve had 2 states: activated or non-activated. Supplying 110 Volts AC (60 Hz) to the solenoid activated the valve. A control switch panel was built grouping all the switches for all the valves. Switches were purchased from APEM part number:12164A3V. They were 3 locking positions, 4 poles switches. The left or the right position of the switch supplied 0 or 5 DC Volts to a Solid State Relay (SSR) SSR240DC10 from Omega. When 5 DC volts was sent to the SSR, it supplied the
necessary 110 Volts to the valve. A green or red electroluminescent light represented the status of the valve (e.g.: open or closed, respectively) on a feed gas flow diagram.

The manual control of the unit consisted of using each switch, located in the control panel, on the right or the left position (closed or open) to control the gas flow. The automatic control was only effective when the switch, relative to the valve, was in the center position (confirmed by a yellow electroluminescent light on the control panel). The valve was monitored then by the computer and could be activated from the computer. Nevertheless, the green and red electroluminescent lights were still representing the status of the valve on the flow diagram. By switching to the middle position, SSR were directly linked to contact relays placed on a board ERB24 purchased from Keithley. These relays provided the 5 DC volts necessary to drive the SSR. A Digital output card PCI PIOSSR48 purchased from Keithley controlled the relays. These relays were necessary since the card PIOSSR48 could not drive the SSR directly. The computer interface for the card was programmed in Labview 5.1 from National Instrument. A dynamic flow diagram was at all times on the computer screen and clicking on the virtual valve would change the valve to the open or closed position.

The main advantage of using solenoid valves instead of manual valve was to prevent the human presence near the balance. The balances were very sensitive to static charges and body mass displacements. The automatic control was programmed to control the valves during the experiment to make reproducible experiments (sample pretreatment and reaction time) or to program an experiment overnight.
3.2.6 Gas Chromatography (GC) Procedures to Verify the Composition of The Reactant Gases and Product Gases during Reaction.

If only testing, Helium should be used as the carrier gas, but when doing an experiment, mixture of He/Hydrogen should be used. This is because the He/H₂ mixture is expensive and should be conserved. The He/H₂ mix is used during an experiment because of the nature of the detector. It is a thermoconductivity (TCD) detector, and the He/H₂ mixture has the highest known thermoconductivity of any mixture, making the TCD a universal detector. This mixture is mainly used in this case to amplify the signal of Hydrogen from the reactant mixture.

The procedures of GC testing are:

1. Check that column (long metal coil) is connected to the TCD.
   
   **NOTE:** This is done by opening the front panel of the GC (there is a button on the bottom right of the front panel) and making sure that the column is not open but screwed in on both ends. The detector (attached to end of column) is on the upper right of the oven chamber, and the sample injector (beginning of column) in on the upper left.

2. Open the carrier gas (He or He/H₂) cylinder and adjust the downstream gauge to 60 psi.

3. Open the knob (turn counterclockwise) for TCD REF so that the carrier gas (REF) will flow through the detector.
4. Also open (counterclockwise) the knob for carrier flow (under purge packed) so that the carrier will flow through the column.

NOTE: It is very important that the TCD is not turned on unless there is gas flow through the detector. If it is open to the atmosphere, (i.e. no carrier gas flow) and the filament is turned on, it will burn out. You can ensure that there is flow though the detector by attaching a bubble flow meter to the (small) detector output on top of the GC. This is a small, copper opening that looks a little bigger than the end of a ballpoint pen.

5. At this point, flow is established through the detector.

6. Turn on GC by toggling switch on bottom right side of the unit. The computer can now be used and the HP Chemstation program on the desktop can be opened. This program has various method files (.MTH) which contain pre-set parameters for operation. You can use one of these methods or you can adjust parameters either on the GC itself or from the computer program.

7. To draw and inject a sample:

The sample panel is directly to the left of the GC and has black, flip switches used to control what goes in/out of the sample box. Before a sample is injected, the sample box must first be evacuated. To evacuate the box, first slowly open the switch that reads MANOMETER. The manometer is to the left of the GC and should at this point be at equilibrium as both ends should be at atmospheric
pressure. However, there is a chance that the sample box may not be at 1 atmosphere which is why the switch should be opened slowly. Next open the VACUUM switch. The box is now open and ready to be evacuated.

8. To evacuate the sample box, turn on the rotary vacuum pump under the GC (red switch). You will hear a bubbling at first, which should then disappear. If it does not disappear, this means that the oil level is wrong in the pump and you should check and change it (use pump manual).

9. You will see the mercury level change in the manometer on the wall to the left of the sample panel. This difference should be at 1 atmosphere (760 mm Hg).

10. To more precisely check the pressure in the sample box, the Macleod gauge should be used (on top of the GC). To open this, there is a black flip switch on a line behind the sample box that must be opened.

11. Let the system pump down until 0.005 mm reads on the Macleod gauge.

12. Once this pressure is obtained, the vacuum flip switch should be closed on the sample panel.

13. Now the sample can be drawn in form the appropriate line. This is done by switching the flip switch for the desired line on the sample panel. The pressure in the manometer should now return to atmospheric on both ends. When each end of the manometer is precisely equal, the flipped switch should be closed.

14. A sample from the selected line is now in the sample box, however, this sample may not be pure as other gases may have been backed up in the lines leading up to the GC. To ensure that you will inject a sample from the reactant mixture into the GC, the lines must be purged a number of times. This is done by simply
evacuating the box ~3 times (repeat steps a-c) and filling it each time with a new sample from the same input.

15. Once the lines have been purged, a fresh sample should be drawn into the sample box (steps a-g). To inject this into the GC, the lever on top of the sample box must be turned approximately a ¼ turn and the START button on the GC immediately pressed.

3.2.7 Experimental Safety Issues

All solenoid 2 way valves, which brought the reactant gases in the system, were normally closed. The 2 way valves for helium and argon were normally opened. Hence, if a power failure happened, hydrogen, methane, carbon dioxide and carbon monoxide would be stopped right after the regulator at the tank and helium and nitrogen would go in every line flushing the system. The maximum flow rate for each gas mixture was 20 cm$^3$/s (STP), based on the turnover rate of the room to ensure that in case of a leak the explosion limit of flammable gases would not be reached.

There are also a number of safety precautions that have been designed for the CVD reactor system. Each of the following elements should be checked and verified before running any experiment:

1. Catch pots for each manometer U-tube:

Each manometer has a catchpot in case of accidental overflow of manometer fluid. Both the manual mass flow controllers have these (red fluid) and the GC Hg manometer (silver...
fluid). Look for these catchpots and make sure they have lines running into them from their respective manometer.

2. Solenoid failure activation states:
All solenoid 2-way valves are configured to be either normally open or closed in case of a power failure:
- He and N₂ → normally open
- All other gases → normally closed.
Reason: if a power failure happened, He and N₂ would go in every line flushing the system, whereas other gases would be stopped right after the regulator at the tank.

3. Emergency shut off switch
The entire unit is equipped with an emergency shut-off switch that will cut the power to the whole system in case of an emergency. This switch is a red button located on the white panel to the right rear of the GC. This button can be pressed if there is an emergency and the experiment needs to be quickly stopped.

NOTE: If this button has been pressed the system may not be able to start when the START key is turned. If this occurs (because the button has been pressed or for any other reason), the breaker switch for the CVD unit is located in the electric panel in the office in 250 Egan. This should be reset and switched to the ON position.

4. Vent
Both the vent and outlet of reactor 1 should eventually lead to a vent on the ceiling above the reactor. Be sure that both tubes are inserted and firmly attached to the vent and that the butterfly valve is open allowing the gases from the pipes to be vented from the room.

5. Toxic & flammable gas detectors

There are detectors in the carbon lab in case of accidental gas leaks.

CO – This is a white box that runs on a 9V battery and is located on the ground near the cylinders in the back of the unit.

H₂ - This is a green and black detector about 1-2 feet long that is located on the work bench near the drill press in the carbon lab. This detector has a charger in the same place that plugs into the wall.

3.3 Characterization of The Resulting Carbon Nanotube Interconnects

There are two types of characterization performed after carbon nanotube network growth: structural characterization and electrical characterization. With structural characterization, it can be determined if the desired structure (i.e., carbon nanotube network between gold electrodes) is achieved. This type of characterization was done by using optical microscope and scanning optical microscope (SEM). The second type of characterization of the resulting carbon nanotube network interconnect is the electrical characterization. With electrical characterization, it can be determined if there is indeed a connection between gold electrodes with this carbon nanotube network – which can be determined by the presence of current flowing from one electrode to another.
3.3.1 Structural Characterization by Optical Microscope and SEM

Structural characterization of the samples was performed by using both optical microscope and scanning electron microscope (SEM). A Hitachi Scanning Electron Microscope, S-4700 CFE (SEM), was used to characterize the thin films deposited as well as the formation of particles, and nanotubes. SEM is a useful tool for general observation of the sample. Samples were directly inserted in the SEM chamber for observation, no pretreatment was necessary. However, sometimes charging could occur on the sample (film too thin to absorb the charging effect of quartz) and a thin coating of chromium (below 1 nm) was necessary to observe the sample. The accelerating voltage typically used was 2 keV with current of 10 μA. The working distance was 3 mm which allowed a point to point resolution of 3 nm.
3.3.2 Electrical Characterization (I-V curve) Using Micromanipulator / Probe Station

Electrical measurements / testing using micromanipulator was performed at the Kostas Center. Electrical characterization of samples was performed by using these steps:

1. Wear safety glasses and gloves
2. Turn on power
3. Turn on optical microscope
4. Move chuck to the closest position to the user
5. Clean (wipe) chuck with isopropanol (IPA)
6. Clean the sides with IPA

Figure 37: Micromanipulator Model 6000 Test Station
7. Cut a small piece of carbon tape (with X-Acto knife) to stick the sample (stick the sample later)

8. Clean the 1st probe (wipe with IPA)

9. Load the 1st probe and screw

10. Clean the 2nd probe (wipe with IPA)

11. Load the 2nd probe and screw.

12. Stick the sample on top of the chuck

13. OR: Stick the sample on the glass slide, then stick the glass slide on the chuck

14. BE CAREFUL: Move the probes (that have been screwed to “ProcessTek Ionaner”)

   CLOSE TO the sample. DO NOT TOUCH THE SAMPLE’S SURFACE

15. Turn on electrostatic machine (Techni-Stat® Ion Transport Model 335PR610)

16. Make sure that the white face (fan) is facing the chuck

17. Connect (pinch) the wristband cable to the electrostatic machine

18. Set the fan to high

19. Wear the electrostatic wristband

20. Bring the sample into LOWEST magnification:

21. Focus the image (the device) by using “coarse focus knob” – disregard the probes’ focus at this time.

22. From now on, NEVER MOVE THE STAGE / CHUCK

23. Move the GREEN objective lens to one side of the gold pads.

24. Change the position of the probe (X, Y) so that it is right in the middle of the gold pad (but DOES NOT TOUCH

25. CLOCKWISE ➔ TIP UP
26. COUNTERCLOCKWISE ➔ TIP DOWN

27. Move the probe SLOWLY downward (turn the knob COUNTERCLOCKWISE), until it touches the gold pad. Remember the trick to make sure that the probe is really touching the gold pad surface!

28. Move the objective lens to THE OTHER side of the gold pads.

29. Change the position of the probe (X, Y) so that it is right in the middle of the gold pad (but DOES NOT TOUCH

30. Move the probe SLOWLY downward (turn the knob COUNTERCLOCKWISE), until it touches the gold pad. Remember the trick to make sure that the probe is really touching the gold pad surface!

31. Connect LEFT red cable to SUM 1 – RED KNOB

32. Connect RIGHT red cable to SUM 3 – RED KNOB

33. Turn on HP 4155A Semiconductor Parameter Analyzer

34. Press MEM4 DIODE VF-IF

35. Click “MEAS”

36. Click “↓”

37. Sweep mode : single ( ➔ DEFAULT)

38. Lin/Log : linear ( ➔ DEFAULT)

39. Start : -1 (then ENTER) ➔ -1 V

40. Stop : 1 (then ENTER) ➔ 1 V

41. Step : 100 mV

42. Press Knob Sweep “Single”
43. THE DATA WILL BE COLLECTED & A GRAPH (Current vs. Voltage) WILL APPEAR

44. Scaling (monitor) ➔ Autoscaling

45. Insert a floppy disk to save the data (txt format)

46. The dimensions of the tungsten probes are as follows:

47. Tip Diameter=5 um

48. Shank Diameter = 25 mil

49. Length = 1.25"

Figure 38 shows the schematic diagram the I-V measurement, while Figure 39 shows the electrical test equipment at Kostas Center [57].
Figure 39: Schematic diagram of probe test station at Kostas Center
(from: 6000 Series Test Station User’s Manual)
4.0 RESULTS AND DISCUSSION

To investigate the *in-situ* growth of carbon nanotube networks for fabricating multiple interconnects at once, patterning techniques are important to place carbon nanotube networks at specific sites. Ideally, the patterning method used for making micro- and nanodevices is e-beam lithography. However, due to some issues regarding this method, another method (i.e., micromasking) was used.

4.1 Issues Regarding E-Beam Lithography

Electron beam lithography (often abbreviated as e-beam lithography) was used to create a nanopattern (troughs) to selectively place nickel nanoparticles as the catalyst of carbon nanotube growth. The initial goals for the e-beam lithography was to create a series of troughs on a Si/SiO₂ substrate. However, there are some issues regarding the use of e-beam lithography, which relate to both pattern generation and post-lithography development. Regarding pattern generation, it was not enough to use the commonly-used “area dose” to create such a small features (~ 20 nm). When the area dose patterning was performed on a substrate with PMMA (which was spin-coated and soft-baked), the desired trough patterns could not be made (see Figure 40). With this soft-bake procedure, the upper layer of PMMA collapsed upon deposition of the thin-film of gold-palladium. This caused the features to be of irregular geometry and size. Some parallel troughs even connected to each other, creating square-shape features.
Some approaches to improve the pattern quality were performed. Those approaches are the uses of ‘line dose’ and ‘hard bake’. By using “line dose”, instead of “area dose”, the trough width can be made as narrow as possible. Furthermore, there would be enough distance between troughs, which would hopefully help prevent troughs from being connected to one another creating squares. Figure 41 shows the resulting pattern made by using line dose. The pattern used was the standard “wheel pattern” used at Kostas Center to test the e-beam dose.
Another approach is by using “PMMA hard bake”, instead of “soft bake”. The procedures of hard-bake were as follows:

- Spin coat PMMA 495K A2 (90 s @ 5000 rpms – thickness ~50 nm)
- Bake on hotplate at 180 °C for 90 s
- Spin coat PMMA 950K A2 (90 s @ 5000 rpms – thickness ~60 nm)
- Bake on hotplate at 180 °C for (90 s + 30 min)

The idea of this hard-bake process was to bake both PMMA 495K A2 (2% PMMA solids in anisole; PMMA molecular mass = 495,000) and PMMA 950K A2 (2% PMMA solids in anisole; PMMA molecular mass = 950,000) for a longer time, so that the PMMA will be denser and harder. Therefore, smaller features can be patterned when the PMMA is exposed to electron-beam, without any PMMA collapse upon deposition of the thin-film of gold-palladium. Figure 42 and Figure 43 show the resulting pattern when PMMA hard-bake process was used. As seen in those figures, troughs with smaller widths were successfully created.
Figure 41: SEM of e-beam lithography pattern created using 2.5 nC/cm (line dose)
Figure 42: SEM of e-beam lithography pattern created using 1 nC/cm (line dose).
Hard bake of PMMA is used
Figure 43: SEM of e-beam lithography pattern created using 4 nC/cm (line dose). Hard bake of PMMA is used

For e-beam lithography where hard-bake process was used, the troughs with ~25 nm width were patterned by using 1 nC/cm line dose. Figure 44 shows the correlation between the e-beam lithography line dose and the width of the resulting trough patterns.
After the issues regarding creating a small pattern were resolved, there were other problems related to the development of the sample after e-beam lithography, especially in the lift-off processes. Even though hard-baked PMMA was better than soft-baked PMMA in terms of the quality of patterned features, it was much more difficult to remove. For PMMA lift-off, the sample was put inside a glass beaker with acetone in it. For soft-baked PMMA, the time needed to lift-off the PMMA layer from Si/SiO₂ was no longer than 24 hours. However, for hard-baked PMMA, even though the sample was left in the acetone for more than 96 hours, there was still PMMA coverage on Si/SiO₂. A possible reason for this difficulty in PMMA removal was that the PMMA was strongly attached to Si/SiO₂ due to the longer baking process (i.e., PMMA hard-bake). The longer the baking time, the more solvent (anisole) is evaporated. As a result, the Van der Waals force
between the polymer (PMMA) and the substrate (Si/SiO₂) increases, resulting in the stronger PMMA adhesion on the substrate.

4.2 Micromasking

Due to the issues related to PMMA lift-off, another method to place nickel nanoparticles on the surface was performed. That method was micromasking in a line pattern and a circle pattern, which are shown in Figure 45 and Figure 46, respectively. For the circle pattern, aluminum foil and transparent plastic film were used as the masks. It was determined that the transparent plastic was better than aluminum foil as the micromasking material in terms of the ease to position the hole. The mask’s hole could be easily placed on top of the gold electrodes’ aperture (Figure 47 and Figure 48). Optical microscope was used to view the gold electrode aperture and to place the mask’s hole right on top of it, so that Ni thin film could be deposited in the desired locations.

![Figure 45: Schematic Diagram of Line Pattern](image-url)
Figure 46: Schematic Diagram of Circle Pattern

Figure 47: Schematic diagram of “micromasking” using Al foil
4.3 Droplet Method

Besides the in-situ growth of carbon nanotubes, a droplet method was also performed in order to place carbon nanotube network between two electrodes. This was done by dispersing carbon nanotubes in ethanol and then depositing a droplet of the suspension on a substrate with a micromask on it (Figure 49 and Figure 50). The main problem in this droplet method was to get similar carbon nanotube coverage area and densities to those in circle pattern in-situ method. Different methods were used to increase nanotube density. One of them was to evaporate some parts of ethanol to get a denser carbon nanotube suspension. Another problem, which is to achieve similar coverage area, could not be solved. The CNT-ethanol suspension covered larger area than the hole area, as the solution spread on the substrate before it evaporated completely, even with the use of vaseline to prevent this spread. The structural and electrical
characterization of both droplet method deposited carbon nanotubes and in-situ grown carbon nanotubes were compared.

Figure 49: CNTs in ethanol
4.4 Structural Characterization of The Resulting Carbon Nanotube Interconnects

The resulting carbon nanotube interconnects prepared by both the grow-in-place (in-situ) and droplet methods were imaged using optical microscope and scanning electron microscope (SEM). Figure 51 and Figure 52 show both optical microscope and SEM images of carbon nanotube interconnect made using droplet method. As shown in those images, the coverage of carbon nanotube network was not uniform. There were some spots that had carbon nanotubes, and there were others that did not (see Figure 51). In Figure 52, the carbon nanotube network coverage looks uniform, because it is just the magnification of one spot that is covered perfectly. The ideal result would have been like this uniform coverage, between gold electrodes. The reason for this phenomenon is because the nanotubes cannot be uniformly suspended in ethanol, even though sonication
of carbon nanotube in ethanol (in a vial) has been done. Another possible reason is the size of droplet which is larger than the mask’s hole. Even with using a syringe with smaller diameter, the droplet size was still bigger than the mask’s hole size.

Figure 51: Optical microscope image of CNN interconnect via Droplet Method
For carbon nanotube interconnects fabricated by in-situ method, the coverage of carbon nanotube network (CNN) was much more uniform compared to those obtained in droplet method. Figure 53 shows the optical microscope image of line-pattern CNN interconnect made using in-situ / chemical vapor deposition (CVD) method. In this figure, it is shown that there are some parts of gold electrodes that were peeled. This was likely due to the high temperature used for in-situ process, which was 900 °C (during nickel thin film annealing / reduction with hydrogen). Figure 54 shows the SEM image of this line-pattern CNN interconnect.
Figure 53: Optical microscope image of CNN interconnect (line pattern) via in-situ / CVD

Figure 54: SEM image of CNN interconnect (line pattern) via in-situ / CVD
For circle-pattern CNN interconnect made using in-situ method, the coverage of carbon nanotube network was also uniform, similar to those from line-pattern. The difference of this circle pattern was that the area of nanotube coverage was smaller compared to line-pattern. This area will determine some variables (such as length) in resistance and resistivity calculation, which will be shown later. Figure 55 shows the optical microscope image of circle-pattern CNN interconnect made using in-situ / chemical vapor deposition (CVD) method. Figure 56 shows the SEM image of this circle-pattern CNN interconnect.

![Optical microscope image of CNN interconnect (circle pattern) via in-situ / CVD](image)

Figure 55: Optical microscope image of CNN interconnect (circle pattern) via in-situ / CVD
The area of carbon nanotube network coverage in this circle pattern was smaller compared to line pattern, hence this pattern is better to be used in in-situ growth of carbon nanotube network for interconnect applications.

4.5 Electrical Characterization of The Resulting Carbon Nanotube Interconnects

Electrical characterization was done by placing a pair of tungsten probes on a pair of gold electrodes (with carbon nanotube network connecting those two electrodes), as shown in Figure 57. With voltages range from -1 V to 1 V with 0.1 V step / increment, data of current flowing from one electrode to another were obtained and then plotted.
Table 6 (Appendix E) shows the Current-voltage measurements of a CNN interconnect via droplet method. Table 7 (Appendix E) shows the average current for each voltage.

![Figure 57: Schematic diagram of I-V measurement](image)

After the data of current were obtained, the next step included plotting the current (I) data versus voltage (V). The slope of the I vs. V curve will determine the resistance of the interconnect (Resistance = 1/Slope). Figure 58 shows the I-V curve of CNN interconnect prepared via droplet method. The I-V curve shows a linear correlation between the currents and voltages, which indicates that the connection shows metallic behavior. The resistance of this CNN interconnect was 281.02 kΩ (calculated from 1/Slope). The error bars represent the standard deviation.
For each electrical measurement, the “control measurement” was also performed. The control measurement is the measurement of currents and voltages between gold electrodes without CNN interconnect. The purpose of this measurement is to show the measurement error from the equipment and to ensure that there were no stray connections between the gold electrodes. Figure 59 shows the control measurement (I-V) for CNN interconnect via droplet method. It is shown that the equipment error is negligible (± 70 nA).

Figure 58: Typical current-voltage relationship of CNN interconnect via droplet method - showing metallic behavior with 281.02 kΩ resistance
Figure 59: Current-voltage between gold pads without CNN interconnect showing equipment error which is negligible (± 70 nA)

Similar electrical measurements were also performed for CNN interconnects fabricated using CVD / in-situ method, both line-pattern and circle-pattern. Table 8 (Appendix E) shows the Current-voltage measurements of line-pattern CNN interconnect via in-situ, and Table 9 (Appendix E) shows the average current for each voltage. The I-V curve shows a linear correlation between the currents and voltages, which indicates that the connection shows metallic behavior. The error bars represent the standard deviation.
Figure 60: Typical current-voltage relationship of CNN interconnect (line pattern) via in-situ / CVD method - showing metallic behavior with 0.47 kΩ resistance
Similar electrical measurements were also performed for circle-pattern CNN interconnects fabricated by using CVD / in-situ method. Table 10 (Appendix E) shows the Current-voltage measurements of line-pattern CNN interconnect via in-situ, and Table 11 (Appendix E) shows the average current for each voltage.

Figure 61: Current-voltage between gold pads without CNN interconnect showing equipment error which is negligible (± 80 nA)
Figure 62: Typical current-voltage relationship of CNN interconnect (circle pattern) via in-situ / CVD method, showing metallic behavior with 107.07 kΩ resistance
Figure 63: Current-voltage between gold pads without CNN interconnect showing equipment error which is negligible (± 175 nA)

After the current vs. voltage for each CNN interconnects were plotted, the next step was to calculate the resistance of each interconnect. The resistance and resistivity were calculated using the following formulas:

$$\text{Resistance (Ohm)} = \frac{\text{Voltage (Volt)}}{\text{Current (Ampere)}}$$

$$= \frac{1}{(\text{Slope of I vs. V curve})}$$

Table 3 shows the comparison between the resistance of carbon nanotube interconnect made with droplet method and in-situ method (line pattern and circle pattern). From that table, it can be seen that the resistances of carbon nanotube network interconnects are greater than the resistances of other interconnects from the literatures (Table 4). The
possible reason of this is the geometry of each interconnect. In carbon nanotube network interconnect, there are lots of nanotubes overlapping each other, creating a network. Therefore, the resistance of that nanotube network is greater compared to that of carbon nanotube bundle and single-carbon nanotube interconnects.

<table>
<thead>
<tr>
<th></th>
<th>Slope (l vs. V)</th>
<th>Resistance (Ω)</th>
<th>Resistance (kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Droplet</td>
<td>3.5585227E-06</td>
<td>2.8101549E+05</td>
<td>281.0154899</td>
</tr>
<tr>
<td>In-situ, line</td>
<td>2.1486742E-03</td>
<td>4.6540327E+02</td>
<td>0.4654033</td>
</tr>
<tr>
<td>In-situ, circle</td>
<td>9.3398751E-06</td>
<td>1.0706781E+05</td>
<td>107.0678129</td>
</tr>
</tbody>
</table>

Table 3: Resistance comparison between droplet method and in-situ (line and circle patterns)

<table>
<thead>
<tr>
<th>Institute</th>
<th>Fujitsu</th>
<th>Samsung</th>
<th>Infineon</th>
<th>SCU &amp; NASA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>MWNT bundles</td>
<td>MWNT bundles</td>
<td>Single MWNT</td>
<td>Single CNF</td>
</tr>
<tr>
<td>Fabrication process</td>
<td><img src="image" alt="Fabrication process" /></td>
<td><img src="image" alt="Fabrication process" /></td>
<td><img src="image" alt="Fabrication process" /></td>
<td><img src="image" alt="Fabrication process" /></td>
</tr>
<tr>
<td>Via diameter [nm]</td>
<td>2000</td>
<td>700</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Via height [nm]</td>
<td>350</td>
<td>1000</td>
<td>150-200</td>
<td>4000</td>
</tr>
<tr>
<td>R [Ω/via]</td>
<td>0.59</td>
<td>1.2 k</td>
<td>7.8 k</td>
<td>9 k (Pd), 13k (Ni)</td>
</tr>
<tr>
<td>Resistivity [Ω·cm]</td>
<td>2.1 X 10⁻³</td>
<td>4.6 X 10⁻²</td>
<td>1.4 X 10⁻³</td>
<td>4.4 X 10⁻⁴</td>
</tr>
<tr>
<td>Max. J [A/cm²/via]</td>
<td>&gt; 2 X 10⁶</td>
<td>---</td>
<td>&gt; 5 X 10⁸</td>
<td>&gt; 1 X 10⁷</td>
</tr>
</tbody>
</table>

Table 4: Comparison of Interconnect Performances by Other Research Group
Electrical resistivity (also known as specific electrical resistance) is a measure of how strongly a material opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electrical charge. Therefore, the lower the resistivity, the better is the material for electrical interconnect applications. Resistivity can be calculated with this formula:

\[
\text{Resistivity} = \frac{\text{Resistance} \times \text{Area}}{\text{Length} (\ell)}
\]

The resistivity of droplet, in-situ (line) and in-situ (circle) are: \(2.49 \times 10^{-1}\ \text{ohm.cm}, 4.12 \times 10^{-4}\ \text{ohm.cm},\) and \(9.49 \times 10^{-2}\ \text{ohm.cm},\) respectively, which are comparable to those of other carbon nanotube interconnects reported in the literatures (Table 4). These resistivity values are still higher than those of some materials (Table 5) [58]. However, the resistivity values in Table 5 are for bulk materials, not in nanometer-scale. As interconnect feature sizes shrink, the resistivity of metal interconnect increases due to surface roughness and grain boundary scatterings [59,60,61].

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity at 20 degree C (Ohm.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>(1.59 \times 10^{-6})</td>
</tr>
<tr>
<td>Copper</td>
<td>(1.72 \times 10^{-6})</td>
</tr>
<tr>
<td>Gold</td>
<td>(2.44 \times 10^{-6})</td>
</tr>
<tr>
<td>Aluminum</td>
<td>(2.82 \times 10^{-6})</td>
</tr>
<tr>
<td>Carbon</td>
<td>(3.5 \times 10^{-3})</td>
</tr>
<tr>
<td>Silicon</td>
<td>(6.40 \times 10^{4})</td>
</tr>
</tbody>
</table>

Table 5: Resistivity Values of Some Materials
5.0 CONCLUSIONS

Carbon nanotubes are a promising candidate to create electronic interconnects for microprocessors due to their low resistivity at nanometer scale, enabling them to achieve high current density (~$10^9$ A/cm², 100 times that of copper). Although carbon nanotube network has a larger overall resistance compared to that of single carbon nanotube, is much easier to grow for creating multiple interconnects at once. The in-situ fabrication of a carbon nanotube network via chemical vapor deposition for on-chip electrical interconnect applications has been demonstrated in this investigation.

Carbon nanotube network (CNN) interconnects were grown between gold electrodes 30 μm apart supported on Si/SiO₂ by combining micropatterning with the controlled growth of carbon nanotubes using nickel catalyst particle placement and a five gas-based CVD reaction. Electrical characterization showed metallic behavior of the carbon nanotube network with a resistance of 281.05 kΩ (droplet method), 0.47 kΩ (in-situ, line), and 107.07 kΩ (in-situ, circle) – which are comparable to the resistivity values reported in literature for other carbon nanotube interconnects.

As interconnect feature sizes shrink, the resistivity of metal interconnect increases due to surface roughness and grain boundary scattering. Therefore, carbon nanotube network promises to replace some materials (e.g., copper), in nanoscale electrical interconnects.
6.0 RECOMMENDATIONS

Some tasks are needed to be done to improve the current fabrication of CNN interconnects. One of them is to find a way to do PMMA lift-off (after e-beam lithography). By using e-beam lithography, much smaller interconnects (e.g., 20 nm-sized) can be obtained. One way to do this is by using a photoresist that is easy to remove during lift-off and – at the same time – does not collapse upon Au-Pd deposition.

Regarding the gold-peeling problem after in-situ growth of carbon nanotube network, it is important to use another chemical vapor deposition method, such as plasma-enhanced CVD, which requires much lower temperature.

The use of four-point probe method [62] is also needed to be performed for more accurate resistance measurements of carbon nanotube network. The key difference between four-point and two-point probe method is that the separation of current and voltage electrodes in four-point probe method allows the ohmmeter/impedance analyzer to eliminate the impedance contribution of the wiring and contact resistances. In other words, the resistance obtained by using two-probe method includes both the carbon nanotube network and the contact resistance between the probe and the sample, while with four-point probe method, the measured resistance is only the resistance of carbon nanotube network.
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57 6000 Series Test Station User’s Manual, Kostas Center for Micro & Nanofabrication, Northeastern University (www.kostas.neu.edu)
8.0 APPENDICES
Appendix A
Gas Flow Calibration Charts and Equations
Manual Mass Flow Controllers

The manual mass flow controllers were calibrated by measuring the pressure drop through a precision-bored Pyrex® capillary tube as it changed linearly with gas flow rate over the ranges used. Each calibration point had an error of roughly ± 0.05 cm³/s due to the use of a stopwatch. Both the backup (test) manual mass flow controller and normal (experimental) mass flow controller sets were calibrated and corrected to Standard Temperature and Pressure. In most cases, the output pressure at the gas cylinder was regulated to 20 psi. Some gases required additional flow, so they were regulated to 30 psi.

He (test), STP

\[ y = 4.22352x + 0.04594 \]

\[ R^2 = 0.99951 \]

He Calibration Curve for Backup System
**N₂ (test), STP**

\[ y = 3.96766x + 0.62584 \]

\[ R^2 = 0.99974 \]

**H₂ (test), STP**

\[ y = 2.57478x + 1.02213 \]

\[ R^2 = 0.99945 \]
CO Calibration Curve for Backup System

CH₄ Calibration Curve for Backup System
CO₂ (test), STP

y = 3.45443x + 0.19895
R² = 0.99961

CO₂ Calibration Curve for Backup System

He (experimental), STP - 30 psi

y = 4.1648x + 2.8201
R² = 0.9994

He Calibration Curve for Experimental System
N₂ Calibration Curve for Experimental System

\[ y = 4.1656x + 0.7135 \]
\[ R^2 = 0.9992 \]

H₂ Calibration Curve for Experimental System

\[ y = 1.4476x + 0.9234 \]
\[ R^2 = 0.9992 \]
CO (experimental), STP - 30 psi

\[ y = 2.88508x + 1.74998 \]

\[ R^2 = 0.99912 \]

Flowrate (cm³/s)

Pressure Drop (cm)

CO Calibration Curve for Experimental System

CH₄ (experimental), STP - 20 psi

\[ y = 2.2467x + 1.0453 \]

\[ R^2 = 0.9995 \]

Flowrate (cm³/s)

Pressure Drop (cm)

CH₄ Calibration Curve for Experimental System

Note:

CO₂ Calibration Curve for Experimental System is not available due to a fouled Brooks Model 8944 mass flow regulator that could not be successfully refurbished.
Digital Mass Flow Controllers (DMFC)

The digital mass flow controllers were calibrated by measuring the pressure drop through a precision-bored Pyrex® capillary tube as it changed linearly with gas flow rate over the ranges used. Each calibration point had an error of roughly ± 0.05 cm³/s due to the use of a stopwatch. Maximum accuracy of the digital mass flow controllers was made possible by setting each controller’s units to be % of total flow. The DMFCs were calibrated and corrected to Standard Temperature and Pressure. In most cases, the output pressure at the gas cylinder was regulated to 20 psi. Some gases required additional flow, so they were regulated to 30 psi. CO₂ has two calibration curves, one to include a low flow rate regime with an MKS controller unit and the other to include the normal flow rate regime using the standard Brooks model 5850E with model 0154E external display.

![DMFC Calibration Curve for H₂](image)

\[
y = 3.60244x - 1.23551 \\
R^2 = 0.99991
\]
DMFC Calibration Curve for CO

$y = 3.78836x - 0.33824$

$R^2 = 0.99959$

DMFC Calibration Curve for CH$_4$

$y = 3.38290x + 1.07612$

$R^2 = 0.99934$
DMFC Calibration Curve for CO₂

MKS Calibration Curve for Very Low Flowrate CO₂
Appendix B
Reactor Temperature Profile
The temperature profile was performed previously by Bazzana with a flow rate of nitrogen of 20 cm³/s (STP) and set so that the isothermal zone was specified between 899 and 900 K. The isothermal zone was found to be at a distance of 2.5 cm beyond the raschig rings and extended for an additional 3.0 cm.

Temperature Profile of the Reactor at 900K with 20 cm³/s (STP) of N₂
Appendix C

Gas Phase Carbon Activity and O/H Ratio Equations
The gas phase carbon activity, \( \hat{a}_c \), was derived as an arbitrary value of the carbon activity, \( a_c \), greater than 1. In the case of graphite, \( a_c \) is equal to 1. Since a mixture of five reactant gases were used, a set of independent equilibrium equations forming graphite were required. Thermodynamic activity is defined to be the component mixture fugacity divided by the fugacity of pure component at 1 atm. Since the system is at high temperature and normal pressures, the gas phase can be considered ideal and the carbon activity is expressed as a function of each of the reaction equilibrium constants, the partial pressures of the reactants and products, and the total pressure (1 atm).

\[
a_i \equiv \frac{f_i}{f_i^o} = \frac{P_i}{P_i^o} \quad (1)
\]

\[
K_i(T) \equiv \prod_i (a_i)^{\nu_i} \quad (2)
\]

\[
2CO \leftrightarrow C_\beta + CO_2 \quad (3) \quad a_c = \frac{K_1(T) \times P_{CO}^2}{P_{CO_2}}
\]

\[
CH_4 \leftrightarrow C_\beta + 2H_2 \quad (4) \quad a_c = \frac{K_2(T) \times P_{CH_4}}{P_{H_2}^2}
\]

\[
CO + H_2 \leftrightarrow C_\beta + H_2O \quad (5) \quad a_c = \frac{K_3(T) \times P_{CO} \times P_{H_2}}{P_{H_2O}}
\]

A value of carbon activity greater than 1 represents a non-equilibrium formation of carbon gas prior to the formation of carbon in the graphite form. By fixing the gas phase carbon activity to a value greater than 1, equations 3, 4, and 5 can be combined.

\[
\hat{a}_c = \frac{K_1(T) \times P_{CO}^2}{P_{CO_2}} = \frac{K_2(T) \times P_{CH_4}}{P_{H_2}^2} = \frac{K_3(T) \times P_{CO} \times P_{H_2}}{P_{H_2O}} \quad (6)
\]
The oxygen to hydrogen ratio is simply a ratio between all of the oxygen species and hydrogen species in each of the five gases.

\[
\frac{O}{H} = \frac{P_{\text{CO}} + P_{\text{H}_2\text{O}} + 2P_{\text{CO}_2}}{2P_{\text{H}_2} + 2P_{\text{H}_2\text{O}} + 4P_{\text{CH}_4}}
\]  

(7)

Finally, the Gibb’s phase rule was applied to ensure that the system is fully specified:

\[
F = N + 2 - \pi - R - S
\]

Where \(N\) is the number of components (H\(_2\), CH\(_4\), CO, CO\(_2\), H\(_2\)O, and C\(_{\text{gas}}\)), \(\pi\) represents the number of phases (gas phase is assumed), \(R\) is the number of independent reactions (there are 3), and \(S\) is the number of independent specifications (\(\dot{\alpha}_c\) and O/H ratio). Thus, in order to fully specify the thermodynamic system, two intensive variables must be fixed. The most convenient intensive variables are temperature and pressure.

In order for the partial pressures to be found, equations 6 and 7 need to be solved simultaneously. The Newton-Raphson method is typically used to solve systems of equations that can be broken down into a single polynomial. Conveniently, a Microsoft Excel spreadsheet has the computational power to solve for the partial pressures in an iterative procedure and screenshots of this spreadsheet are provided in the following pages.
Microsoft Excel is a powerful spreadsheet tool that can be used to automate calculations. By following the instructions provided on the right side of the spreadsheet, the spreadsheet will provide the DMFC settings to input so that the appropriate flowrate of each gas is delivered to the reactor. The spreadsheet incorporates calibration curves for both the manual manometer and DMFC systems. It also incorporates reaction equilibrium curves for all three independent graphite forming gas phase reactions. These curves are embedded into the equations for each equilibrium constant cell. By inserting the reaction temperature desired, the equilibrium constants will update automatically based on the new temperature. The iterative procedure used is the tool, Solver. Solver allows input of additional constraints like $\hat{a}_c$ and O/H ratio. There are additional embedded equations that will warn the user when to install the MKS unit for the CO$_2$ DMFC. Equilibrium constants were provided from previous work done by Bazzana [Error! Bookmark not defined.], however, they can alternatively be found in the NIST-JANAF Thermochemical Tables. In order to provide for good interpolation approximations, the equilibrium constant data was fitted to a 6$^{th}$ order polynomial within the range of the data. Finally, saturated steam psychrometric data were also provided from previous work [Error! Bookmark not defined.] and can alternatively be found in standard chemical engineering thermodynamics textbooks such as Smith, J.M., H.C. VanNess, and M.M Abbott, Introduction to Chemical Engineering Thermodynamics 6$^{th}$ Ed., McGraw Hill, New York, 2001. This data was used to calculate the appropriate water bath temperature to produce the correct partial pressure of water to saturate the feed gas stream according to the experiment parameters.
<table>
<thead>
<tr>
<th>Column</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>The Experiment</td>
</tr>
<tr>
<td>B</td>
<td>Given Data</td>
</tr>
<tr>
<td>C</td>
<td>T (K)</td>
</tr>
<tr>
<td>D</td>
<td>H₂ (mol%)</td>
</tr>
<tr>
<td>E</td>
<td>CO (mol%)</td>
</tr>
<tr>
<td>F</td>
<td>CH₄ (mol%)</td>
</tr>
<tr>
<td>G</td>
<td>CO₂ (mol%)</td>
</tr>
<tr>
<td>H</td>
<td>H₂O (mol%)</td>
</tr>
<tr>
<td>I</td>
<td>Methane Conversion</td>
</tr>
</tbody>
</table>

Instructions for Mole Fraction Solver:
1. Type in Desired Temperature in Kelvin.
2. Type in P (atm) and Flow Rate (ccps) if experiment calls for an update.
3. The Equilibrium Constants should change to complement the Desired Temperature automatically.
4. Click “Tools”
5. Click “Solver…”
6. Set Target Cell: “Total” ($B$24) = $E$24 = Value of 1
8. Subject to the Constraints:
   a. “Total” – $E$24 ≤ 1
   b. “H₂” ≤ $E$24 ≤ “CO”
9. Click “Solve”

In the event of a somewhat incorrect solver guess, keep the proposed solution anyway and manually change the offending negative composition to a positive more reasonable value such as 0.01. Click “Solve” in Solver once again, and it should guess correctly.

Bolded values can be changed depending on experimental goals.

DO NOT MANUALLY CHANGE ANY CELLS IN BLUE AS THEY ARE CALCULATED BY FORMULA.
Equilibrium Constants Corresponding to all Three Independent Reactions as a Function of Temperature Fitted to 6th-order Polynomial Equations to allow for good interpolation approximations
Saturated Steam Data where inverse temperature is plotted as a function of the natural logarithm of vapor pressure

\[
\frac{1}{T} = -1.9265441898 \times 10^{-4} \ln(P_{\text{VAP}}) + 3.5745390878 \times 10^{-3}
\]

\[R^2 = 0.99988\]

Saturated Steam Values
Appendix D

Summary of Experimental Variables and Results
Various reactor conditions and nickel thin-film thicknesses were studied in order to better understand the conditions that allowed for preferential growth of straight multi-wall carbon nanotubes. In all experiments, the nickel nanoparticles were formed on the substrate after an annealing process where the sample was exposed to flowing hydrogen gas at 20 cm³/s (STP) for 5 min. at a temperature of 1173 K. Additionally, all of the carbon growth processes occurred at 900 K, a gas phase carbon activity of 20, and overall flow rate of 20 cm³/s (STP) for 90 minutes. The only variables that were altered were the O/H ratio and the thickness of the initial nickel thin-films.

<table>
<thead>
<tr>
<th>Mass of Ni (mg) (± 0.01 mg)</th>
<th>Thin-film thickness (nm) (±10%)</th>
<th>Nanoparticle Diameter (nm)</th>
<th>O/H Ratio</th>
<th>Resulting MWCNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>1.49 – 1.51</td>
<td>10.2</td>
<td>0.1</td>
<td>Spaghetti</td>
</tr>
<tr>
<td>1.8</td>
<td>1.49 – 1.51</td>
<td>10.2</td>
<td>0.5</td>
<td>Both</td>
</tr>
<tr>
<td>0.5</td>
<td>0.59 – 0.61</td>
<td>6.1</td>
<td>0.5</td>
<td>Straight</td>
</tr>
</tbody>
</table>

Summary of Experimental Variables and the Resulting Morphology of the Multi-wall Carbon Nanotubes
### Appendix E

Electrical Characterization Results

<table>
<thead>
<tr>
<th>Voltage, V (V)</th>
<th>Current, I (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
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<td>-3.19E-06</td>
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</table>

Table 6: Current-voltage measurements of CNN interconnect via droplet method
<table>
<thead>
<tr>
<th>Voltage, V (V)</th>
<th>I average (A)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>-3.53079E-06</td>
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<td>2.7312E-08</td>
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</table>

Table 7: Average current for each voltage – CNN interconnect via droplet method
<table>
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<tr>
<th>Voltage, V (V)</th>
<th>Current, I (A)</th>
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</thead>
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<td>-0.0020799</td>
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<td>-0.0018484</td>
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<td>-0.0013861</td>
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<tr>
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<tr>
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<tr>
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<tr>
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<td>-0.00023088</td>
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<tr>
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<td>2.6E-08</td>
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<td>0.00046223</td>
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<tr>
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<tr>
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<tr>
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<td>0.0011554</td>
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<tr>
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<td>0.0013865</td>
</tr>
<tr>
<td>0.7</td>
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<td>0.0020801</td>
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<tr>
<td>1</td>
<td>0.0023115</td>
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</table>

Table 8: Current-voltage measurements of CNN interconnect (line pattern) via in-situ / CVD method
<table>
<thead>
<tr>
<th>Voltage, V (V)</th>
<th>I average (A)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>-0.00214979</td>
<td>0.00024314</td>
</tr>
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Table 9: Average current for each voltage – line-pattern CNN interconnect via in-situ
Table 10: Current-voltage measurements of CNN interconnect (circle pattern) via in-situ / CVD method

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Table 11: Average current for each voltage – circle-pattern CNN interconnect via in-situ