GOLD NANOPARTICLE DECORATED CARBON NANOTUBE FIELD EFFECT TRANSISTORS FOR GLUCOSE AND GAS SENSING

A Dissertation
submitted to the Faculty of the
Graduate School of Arts and Sciences
of Georgetown University
in partial fulfillment of the requirements for the
degree of
Doctor of Philosophy
in Physics

By

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Washington, DC
August 19, 2014
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Abstract

The research presented in this thesis focuses on the fabrication, functionalization and characterization of carbon nanotube field effect transistors (CNTFETs) with gold (Au) nanoparticles for gas and glucose sensing applications.

Carbon nanotube field effect transistors are made of an individual carbon nanotube (CNT) in this work. Carbon nanotubes are synthesized using chemical vapor deposition (CVD) on a p-doped silicon/silicon oxide substrate. This process provides mostly single-walled carbon nanotubes (SWCNTs) that are either metallic or semiconducting. Au is deposited onto the carbon nanotube using electron-beam lithography to make source and drain electrodes. Electrical characterization is performed using software controlled pico-amp meter/DC voltage source connecting to a four-probe micromanipulator system.

A simple in-situ electrochemical method to target the deposition of gold, as well as other metallic nanoparticles along a CNTFET is introduced in this research. The transistors are passivated by a thin layer of poly(methyl-methacrylate), or PMMA. Areas of the PMMA along the carbon nanotube are exposed using electron-beam lithography to target the locations where Au nanoparticles need to be placed. An appropriate potential difference is applied between an in-situ sacrificial gold electrode and the CNT, all immersed under a droplet of electrolyte solution. By adjusting the applied voltage and time of deposition, the size of the Au nanoparticle can be
controlled from 10 nm to over 100 nm. This method provides better control and is much easier to carry out compared to other site-specific deposition techniques. Such decorated Au nanoparticle/CNTFET heterostructures will allow for a better understanding of CNTFET gas sensing behavior, as well as finding application in site-specific biomolecule anchoring for the development of highly sensitive and selective biosensors, which will be demonstrated in this research work.

This research suggests that when a Au nanoparticle is deposited onto a semiconducting CNT, a local Schottky barrier is created on the CNT side wall. This Schottky barrier changes when exposed to gas molecules, which is the main mechanism for gas sensing of the CNTFET. For glucose detection, Au nanoparticles provide a preferable orientation of the glucose oxidase molecules, which potentially facilitates the electron transfer between glucose oxidase and the CNT.
Acknowledgements

I would like to thank the following people who helped along the way:

Professor Makarand Paranjape for giving me the opportunity to join his group, allowing me to conduct various interesting research projects, helping me in all the time of research and writing of this thesis, and providing continuous support throughout the course.

Professor Paola Barbara, Professor Amy Liu, and Professor Yuye Tong for being my committee members, and willing to spend their time to support and guide me on the research project.

Professor Marcio Fontana for his collaboration on multiple projects, and his delicious caipirinha.

Professor Faye Rubinson for the helpful discussions about glucose oxidase and glucose detection.

Dr. Jianyun Zhou for mentoring me entering the lab and all the help afterwards.

Dr. A. Jasper Nijdam for his anecdotes, his help in the lab, and maintaining a good working environment in the lab.

Leon Der for the help with all the experiment set ups and gadgets when I needed them.

Dr. Yanfei Yang, Dr. Mohamed Rinzan, Dr. Anthony Boyd for the discussions that helped me in both fabrication and in understanding the physics of carbon nanotube devices.

Dr. Mbi Armstrong, Dr. Isha Dube for their help and support throughout grad school.

Dr. Xinran Zhang for his help with using the atomic force microscope.

The Physics Department for supporting my research and providing funds.
Finally, I would like to thank my parents for their love, support, and encouragement.

Many thanks, this would not be possible without you.

Yian Liu
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CHAPTER 1
BACKGROUND

Since their discovery in 1991[1], carbon nanotubes (CNTs) have shown potential applications in the field of nanotechnology due to their remarkable electrical, mechanical, thermal and chemical properties. Recent advances in nanotechnology enabled the development and use of carbon nanotubes as field effect transistors (FETs). In this chapter, background of carbon nanotubes and carbon nanotube field effect transistors (CNTFETs) is given.

1.1 Carbon Nanotubes and Their Applications

Carbon nanotubes possess excellent electronic properties. Based on the structure of the carbon nanotubes, they can be either metallic or semiconducting. Metallic carbon nanotubes can be used to replace the metal lines in integrated circuits due to their small size and high current density [2]. On the other hand, semiconducting carbon nanotubes have shown great potential to be used to build transistors that scale smaller than silicon based metal oxide semiconductor field effect transistors (MOSFET) in integrated circuits [3].

Other than their excellent electrical property, carbon nanotubes also possess outstanding mechanical properties. Due to the covalent \( sp^2 \) bonds formed between the individual carbon atoms, carbon nanotubes have the highest tensile strength of any known materials [4], while the \( \pi \) bond allows electrons to move easily across the molecule plane. A diagram of the carbon bond in carbon nanotube is shown in Figure 1.1. Carbon nanotubes are also extremely elastic that can sustain large strains under pressure. Such mechanical properties have led carbon nanotubes to
applications such as polymer composites such as the material for ice hockey sticks [5], and nanoprobes such as tips for atomic force microscope probes [6].

![Diagram of carbon-carbon bond in carbon nanotubes](image)

**Figure 1.1.** Carbon-carbon bond in carbon nanotubes; $sp^2$ bond, or $\sigma$ bond sits in the molecule plane while the $\pi$ bond is perpendicular to the molecule plane

Other applications of carbon nanotubes have also been investigated. For example, carbon nanotubes have been utilized in energy applications due to their unique electrical properties and high surface to volume ratio. Researches have suggested that carbon nanotubes have the potential to be used as the electrodes in flexible lithium-ion batteries [7]. Carbon nanotubes have been used as tiny cooling elements due to their excellent thermal conductivity [8]. They have also been utilized as field emitters due to their low threshold voltage and good emission stability [9]. In fact, research on the influence of argon on field emission properties of the CNTs during growth has been studied by our group [10] and details will be provided in Appendix A.
1.2 Carbon Nanotube Sensors

Carbon nanotubes have shown great promise as sensing elements that take advantage of their outstanding properties. For example, Fung et al. [11] reported a thermal sensor that used bundles of carbon nanotubes as sensing elements. Robinson et al. [12] developed a carbon nanotube network capacitor for gas sensing applications. Wood and Wagner [13] proposed that carbon nanotubes can be used as molecular and macroscopic pressure sensors. Kong et al. [14] demonstrated that semiconducting carbon nanotubes can act as sensitive chemical sensors.

Among all the diverse sensing applications, one approach is to fabricate semiconducting carbon nanotubes as the channels of field effect transistors devices. The carbon nanotube also acts as sensing element being extremely sensitive towards minute variations in surrounding environment. Extensive research has focused on utilizing carbon nanotube field effect transistors in bio-sensing and gas-sensing applications [15].

In addition, carbon nanotube field effect transistors can be functionalized by various means to achieve better sensing sensitivity and selectivity. For example, different antigens have been bound to the carbon nanotubes to selectively detect certain antibodies [16]. Other work has shown that CNTFETs can be coated with polymers to selectively bind to bio molecules [17]. One promising way to functionalize CNTFETs is to decorate them with gold (Au) nanoparticles. Au nanoparticle is the most widely used metal nanoparticle, especially in bio sensing applications due to its biocompatibility, excellent electron conductivity, extraordinary optical properties, and the ability to bind with thiols, a class of organic chemical compounds that contains a carbon-bonded sulphhydryl group that is often used as linking molecules [18].
In this research, we study the functionalization of CNTFETs through controlled deposition of Au nanoparticles for glucose and gas sensing applications. Details about carbon nanotube synthesis, carbon nanotube field effect transistor fabrication and Au nanoparticle decoration will be given in Chapter 2 and Chapter 3.

1.3 Structure of Carbon Nanotubes

The structure of carbon nanotubes can be considered as rolled-up graphene sheets, consisting of a hexagonal lattice arrangement of carbon atoms. The rolling of the graphene sheet can occur along an axis called the chiral vector, as shown in Figure 1.2. The resulting diameters of the hollow cylinders range from 1 nm to hundreds of nanometers [19]. The cylinders can be made from a single layer of graphene, termed as single-walled carbon nanotubes (SWCNT), or multiple concentric graphene layers, called multi-walled carbon nanotubes (MWCNT). An example of a double-walled carbon nanotube is shown in Figure 1.3.
The rolling of the graphene sheets can occur along different chiral vectors. These chiral vectors are represented by \( \mathbf{C} = m \mathbf{a}_1 + n \mathbf{a}_2 \), with \( m \) and \( n \) being the number of the unit vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) along the two directions in the crystal lattice of graphene, as shown in Figure 1.4
The index \((m, n)\) is then used to differentiate between the types of carbon nanotubes. The graphene sheet can be wrapped along one of the symmetry axis: this gives either a zig-zag tube \((n, 0)\) or an armchair tube \((n, n)\). It is also possible to roll the sheet in a direction that differs from a symmetry axis and obtain a chiral nanotube \((n, m)\). The three types of chiralities of CNT are shown in Figure 1.4 (b).

\[
\begin{align*}
\text{Figure 1.4. (a) Graphene sheet and carbon nanotube chiral vectors (m, n) with corresponding chiralities (b) Models of SWNTs with different chiralities}
\end{align*}
\]

The diameter of the carbon nanotube, \(d\), is given by \(L/\pi\), where \(L\) is the circumferential length of the carbon nanotube:

\[
\begin{align*}
L &= |C| = a\sqrt{m^2 + n^2 + mn} \quad (1) \\
d &= L/\pi \quad (2)
\end{align*}
\]

\(a\) is the lattice constant and it is given by:

\[
\begin{align*}
a &= \sqrt{3}a_{c-c} = \sqrt{3} \times 1.44 \text{ Å} = 2.49 \text{ Å} \quad (3)
\end{align*}
\]

where \(a_{c-c} = 1.44 \text{ Å}\) is the carbon-carbon bond length.
The structure of a carbon nanotube strongly affects its electrical properties. Depending on the chirality, carbon nanotubes can be metallic, semimetallic or semiconducting. A single-walled carbon nanotube is metallic when \( n = m \). If \( n - m = 3i \) (\( i \) being an integer), the carbon nanotube is semimetallic with a very small band gap. These carbon nanotubes can be considered as metallic in room temperature. In all other cases, the carbon nanotube is semiconducting [20]. Thus, about one-third of the carbon nanotubes are metallic. The magnitude of the band gap for the semiconducting carbon nanotubes is proportional to the inverse of the tube diameter, giving each carbon nanotube’s unique electronic properties [20]. The difference in their electronic properties can lead to different applications. Metallic carbon nanotubes are widely used in composite materials to enhance the overall electrical and thermal conductivity, while semiconducting carbon nanotubes are often used in field effect devices for sensor applications.

### 1.4 Carbon Nanotube Field Effect Transistors

A carbon nanotube field effect transistor uses either a single carbon nanotube or a network of carbon nanotubes as the channel material. Similar to traditional field effect transistors, a carbon nanotube field effect transistor uses an electric field to control and modulate the electric current flows along the carbon nanotube.

A CNTFET typically consists of one or more carbon nanotubes, two metallic electrodes contacting the carbon nanotubes, serving as source and drain, an insulating dielectric layer on top of or underneath the carbon nanotube, and a conductive gate within a few hundred nanometers to the carbon nanotube but insulated by the dielectric layer. The conductivity of the CNT(s)
between the source and drain electrodes can be modulated by a voltage applied to the gate. There are many types of CNTFET based on the type of gate. The most common types are given below.

1.4.1 Back Gate Carbon Nanotube Field Effect Transistors

A back gate CNTFET utilizes a dielectric layer underneath the carbon nanotube channel to insulate the carbon nanotubes from the gate substrate. A schematic diagram of a back gate CNTFET is shown in Figure 1.5. A Source/Drain (S/D) voltage ($V_{SD}$) is applied to the metal contacts. A gate voltage ($V_G$) is applied to the back gate to control the conductivity of the carbon nanotube channel between the source and drain electrodes.

![Diagram of a back gate CNTFET](image)

Figure 1.5. Diagram of a back gate CNTFET

Back gate CNTFETs are relatively easy to build. Silicon oxide and a doped silicon substrate are commonly used as the dielectric layer and back gate, respectively.
1.4.2 Top Gate Carbon Nanotube Field Effect Transistors

Top gate CNTFETs have been developed based on the structure of back gate CNTFETs. Instead of using the dielectric layer and gate beneath the CNT, the dielectric layer and the gate are deposited on top of the CNT. A schematic diagram of a top gate CNTFET is shown in Figure 1.6.

Top gate CNTFETs have two advantages. First, the thickness of the dielectric layer on top of each CNTFET can be controlled specifically during the deposition process, enabling flexible fabrication. Second, for a multiplicity of CNTFETs residing on the same substrate, each device can have its own independent gate allowing the application of different gate voltage for different CNTFETs. This is in contrast to back gate device, where only one gate voltage can be applied to multiple CNTFETs since all gates are shared by the common substrate. Thus, top-gated CNTFETs provide more flexible control for multiple devices.
1.4.3 Suspended Carbon Nanotube Field Effect Transistors

Suspended CNTFETs were first developed by Dai’s group [21], where a carbon nanotube is suspended over a trench between the two electrodes. Air or vacuum is used as the dielectric layer. A schematic diagram of a suspended CNTFET is shown in Figure 1.7.

Since the carbon nanotube is not in contact with the substrate or the oxide layer, the suspended CNT geometry can reduce the scattering at the CNT-substrate/oxide interface. Therefore, suspended CNTFETs are ideal for probing the intrinsic electrical properties of nanotubes [21].

1.5 Principle of Operation for Carbon Nanotube Field Effect Transistors

The principle of operation can be generally divided into two parts: the property of the metal-CNT junction, and the function of the gate voltage.
1.5.1 Schottky Barrier at the Metal-Carbon Nanotube Junction

A CNTFET is considered to be a Schottky barrier (SB) device since charge transport in the CNT channel is controlled by the Schottky barrier formed at the contacts. When contact is made between the CNT and the metal electrodes, a potential barrier is formed at the metal-CNT junction. At steady state, this barrier blocks the current flow across the interface when a voltage is applied between source and drain. This barrier is called Schottky barrier. The height of the SB ($\Phi_{SB}$) is the difference between the majority carrier band edge of the semiconducting CNT and the metal Fermi level across the metal-CNT interface. For an $n$-type CNTFET, the SB height is the difference between the conduction band minimum and the metal Fermi level ($E_{FM}$). For a $p$-type CNTFET, the SB height is the difference between the valence band maximum and the metal Fermi level. Initially, the unaligned Fermi levels of the metal and CNT begin to line up due to charge redistribution to achieve the electrical equilibrium. This Fermi level alignment causes a bending in the bands for the semiconducting CNT. The band bending diagram is shown in Figure 1.8, with $E_{FM}$ and $E_{FC}$ being the Fermi level of metal and CNT respectively. The heights of the Schottky barriers for both $n$-type and $p$-type CNTFETs are shown in Figure 1.8, with $\Phi_{SB}$ representing the height of the Schottky barrier.
1.5.2 Function of the Gate Voltage in Carbon Nanotube Field Effect Transistors

The gate of a CNTFET works to modulate the contact resistance by changing the width of the Schottky barrier at the metal-CNT junction. The change of gate voltage changes the electrostatic potential in the CNT and therefore bends the energy band of the CNT. In general, a
positive gate voltage shifts the Fermi level of the CNT towards the conduction band. Since the Fermi level of the CNT always lines up with the Fermi level of the metal, the positive gate voltage bends the band downward. On the contrary, a negative gate voltage shifts the Fermi level towards the valence band and therefore bends the band upward.

Taking a p-type CNTFET as an example (band diagram is shown in Figure 1.9), when zero gate voltage is applied, there is no current flow since the Fermi level lies inside the band gap (dotted line in Figure 1.9). When a small positive gate voltage is applied, the band is bent downward a small amount. Since the Fermi level still lies inside the band gap, there is no current flow. Therefore the device remains off (Figure 1.9 (a)). When a sufficiently large positive gate voltage is applied, the band bends further downward and the Fermi level is brought into the conduction band, allowing electrons to flow. However, due to the large width of the Schottky barrier, few electrons can tunnel through, resulting in a very large contact resistance (Figure 1.9 (b)). Therefore the device is still effectively off. On the other hand, when a small negative gate voltage is applied, the band is bent upward, bringing the Fermi level into the valence band. The width of the Schottky barrier is small in this case, enabling electron tunneling current (Figure 1.9 (c)). The device is now turned on. A large negative gate voltage can further bend the band upward, effectively decreasing the width of the Schottky barrier even more and thus, increasing the source/drain current (Figure 1.9 (d)).
Figure 1.9. Band bending induced by (a) small positive gate voltage (b) large positive gate voltage (c) small negative gate voltage (d) large negative gate voltage
1.6 Advantages of Carbon Nanotube Field Effect Transistors

CNTFETs can be used as nano-sensors due to their small size and their semiconducting nature. Adsorption of molecules onto the carbon nanotube surface can cause depletion or accumulation of charges. Therefore, detection can be observed as a change in conductance between source and drain electrodes. CNTFETs have many advantages as nano-sensors. First, because of their semiconducting nature, CNTFETs can easily transduce the interaction between the nanotube and molecules into an amplified electronic signal. Second, carbon nanotubes are comparable in size to biological molecules, ensuring appropriate size compatibility between the detector and the detected species [22]. In addition, all carbon atoms are on the surface of the CNT, allowing direct contact and interaction with the molecules in the environment. This feature, together with its 1-D structure makes the conductance of the CNTFET very sensitive to the local environment. Any local disturbance could dramatically change the carrier concentration along the carbon nanotube, resulting in fast detection and high sensitivity [20]. In this research, a back gate geometry is used for the CNTFETs for glucose and gas molecule sensing due to its simplicity. The fabrication and characterization of the CNTFETs will be given in Chapter 2.
CHAPTER 2
DEVICE DESIGN, FABRICATION AND CHARACTERIZATION

In this research, a back gate configuration is used as was detailed in Chapter 1, and the fabrication overview is given. A schematic diagram is shown in Figure 2.1(a), where a heavily doped silicon substrate capped with an oxide layer, is used as the substrate, serving as the gate and insulating dielectric, respectively. Carbon nanotubes are grown on the substrate and lie parallel to the surface. Gold electrodes are used to make contact with the carbon nanotube, since gold makes good contact with CNTs due to a good wettability and has high electrical conductivity. A scanning electron microscope (SEM) image of a typical carbon nanotube field effect transistor is shown in Figure 2.1(b).

Figure 2.1. (a) Schematic representation of a carbon nanotube field effect transistor (b) SEM image of an actual carbon nanotube field effect transistor

From the basic device composition given above, there are three important aspects of the process: 1. Carbon nanotube synthesis; 2. Electrode design and deposition; 3. Electrical
Characterization. This chapter elaborates upon the various aspects related to device fabrication, and the process is given in detail in the following sections.

2.1 Carbon Nanotube Synthesis

The carbon nanotube synthesis is based on the process reported by another group [23]. Catalytic chemical vapor deposition (CVD) of a gaseous carbon feedstock over metal catalysts is used to produce carbon nanotubes. Catalysts are prepared in liquid form and patterned using lithographic techniques. Details about carbon nanotube synthesis are discussed below.

2.1.1 Catalyst Preparation

Catalyst is very critical to carbon nanotube synthesis. Research groups have used metallic Fe, Co, and Ni as catalyst materials for carbon nanotube growth. Bimetallic catalysts have also been used because they have an additional effect on the outcome of the carbon nanotube growth. Researchers have reported that an addition of Mo into a Fe-based catalyst is very effective in producing single-walled carbon nanotubes, and lowering the growth temperature and hydrocarbon flow [24, 25]. In addition, additional materials are used to support and hold the catalyst in their patterned locations, resulting in well-defined growth sites for the CNTs. Support materials can improve the yield of CNTs by providing an extremely large surface area, as shown in Figure 2.2. Support materials are also found to play an important role on the outcome of the carbon nanotubes. Alumina (Al₂O₃) supported catalysts are found to produce mostly individual SWCNTs, while silica (SiO₂) supported catalysts lead to bundles of carbon nanotubes [24].
In this research, a Fe/Mo bimetallic catalyst is used supported by Al$_2$O$_3$ nanoparticles. The molar ratio of the two metals is adjusted to obtain a desired carbon nanotube density. The actual molar ratio is kept constant at Fe: Mo = 100: 55. The concentration of Al$_2$O$_3$ nanoparticles is chosen so that the catalyst islands form well-defined shapes and could be clearly seen with an
SEM, even when there is photoresist on top of the catalyst islands (these catalyst islands will be covered with photoresist and serve as alignment marks for electron-beam writing in later fabrication steps). Methanol, ferric nitrate nonahydrate (Fe(NO$_3$)$_3$•9H$_2$O), and Molybdenum diacetylacetonate dioxide (MoO$_2$(acac)$_2$) are all purchased from Alfa Aesar. The recipe of the catalyst is as follows [24]:

1. Measure 1.6 mg of Fe(NO$_3$)$_3$•9H$_2$O and 0.5 mg of MoO$_2$(acac)$_2$.
2. Dissolve in 20 ml methanol.
3. Add 15mg of Al$_2$O$_3$ nanoparticles to the methanol solution.
4. Sonicate the solution for one hour

This recipe has been experimentally shown to provide mostly semiconducting single walled carbon nanotubes that are suitable for this research.

2.1.2 Catalyst Patterning

In order to ensure that carbon nanotubes grow from specific locations, the catalyst is deposited as isolated micrometer-sized islands at precisely patterned locations on the substrate. These catalyst islands not only catalyze the nanotube growth and define their locations, but also serve as alignment marks for subsequent source and drain electrode patterning. Both photolithography and electron beam (e-beam) lithography have been used to pattern the catalyst. The two methods will be discussed below.

2.1.2.1 Substrate Preparation
The commonly used substrate for CNTFETs is doped silicon with an oxide insulating layer. In this project, a box of 4-inch, 500-550 µm thick boron doped Single Side Prime (SSP) Grade silicon wafers (with a 300 nm insulating layer of SiO$_2$ grown on the doped silicon by dry thermal oxidation) are purchased from Nova Electronic Materials Ltd, Flower Mound, TX. The resistivity of the doped silicon is 0.001-0.005 Ohm·cm. The wafers are cleaved into 10 mm × 7 mm small chips. Then the small chips are cleaned by sonicating in trichloroethylene (C$_2$HCl$_3$), acetone ((CH$_3$)$_2$CO), and isopropanol (C$_3$H$_8$O) sequentially, each for 2 min, and then rinsed with isopropanol and dried with nitrogen before use.

2.1.2.2 Catalyst Patterning Using Photolithography

Photolithography is the most widely used lithographic method used in Micro/Nano-electromechanical systems (MEMS/NEMS) processing. Photolithography uses a UV light source and a mask to transfer the pattern on the mask to a light sensitive polymer called photoresist (Figure 2.3). There are two kinds of photoresist, positive photoresist and negative photoresist. When positive photoresist is exposed to the UV light, the bonds in the polymer break and easily dissolved in developer. In contrast, the negative photoresist will crosslink and remain intact on the substrate after UV light exposure and development.
In this research, a Karl Suss MJB-3 photo mask aligner is used. (Figure 2.4) This model produces an UV light of 340 nm wavelength and 19 mJ/cm² power. The photoresist used here is SU-8: 2, which is an epoxy-based negative photoresist, where 2 denotes the viscosity of the solution. The lower the number, the less viscous, and it typically refers to the thickness achieved when spun at 4000 rpm. SU-8 is a widely used photoresist in microfluidic and MEMS applications. In fact, our group has proposed and fabricated a micro-cantilever structure based on SU-8 and a piezoelectric polymer for bimolecular detection. Details about this are given in Appendix C. SU-8: 2 is purchased from MicroChem Corp. Newton, MA and is diluted to achieve a 500 nm thickness. The mask is a quartz plate with chromium pattern on it. A photo of the mask and an optical microscope image of the pattern on the mask are shown in Figure 2.5. The pattern of the carbon nanotube catalyst islands printed on the mask consists of a five by three matrix. Each element of the matrix has five catalyst islands, which is shown in the inset in Figure 2.5.
Figure 2.4. A picture of the Karl Suss MJB-3 photo mask aligner

Figure 2.5. A picture of the photo mask showing multiple patterns for different applications; inset shows an optical microscope image of the pattern (one element of the matrix that has five catalyst islands) and one L shaped alignment mark on the mask
A spinner is used to spin coat the photoresist onto the SiO₂/Si substrate. Other than SU-8, another photoresist, Poly methyl methacrylate (PMMA) is also used. This PMMA layer can be dissolved in acetone and will serve as a release layer to lift off the SU-8 layer. PMMA 950 C2 is purchased from MicroChem Corp, Newton, MA. Here 950 refers to the molecular weight of this PMMA, where C2 refers to the solvent used, namely 2% chlorobenzene. PMMA and SU-8 are spin coated onto the substrate at different spin rates. The samples are then exposed to UV light after a pre-exposure bake. Here an immersion technique is used, which is a method used in photolithography to increase the resolution of the pattern. It involves putting a small drop of water between the mask and the sample. Since water has a larger refractive index than air, the wavelength of the light is effectively decreased in water, resulting in better pattern resolution. After a post-exposure bake, the samples are immersed in SU-8 developer to remove any unexposed SU-8, thereby exposing the underlying PMMA layer, which is unaffected by the developer. The exposed PMMA is then removed by reactive ion etching (RIE), which is a dry etching technology commonly used in silicon fabrication processing. It uses a plasma, initiated by a strong radio frequency electromagnetic field to remove the material on the substrate. Different chemistries for plasmas are used to etch different materials. For PMMA, a O₂ plasma is used, and once it is removed, the pattern on the mask is successfully transferred to the substrate. A detailed photolithography patterning process follows, and is schematically illustrated in Figure 2.6.

1. Cut samples to size needed, 7 X 10 mm.
2. Clean chips in TCE, acetone, and IPA with a 2 minutes sonication in each solvent.
3. Spin PMMA 950 C2 at 3500 rpm for 45 sec. After spinning, put chips on a flat plate.
4. Bake at 180°C for 2 min on a hotplate.

5. Spin SU-8: 0.5 (made by diluting SU-8: 2) at 4000 rpm for 45 sec.

6. Bake on top shelf of oven at 90°C for 10 min.

7. Expose for 3.5 seconds using immersion techniques at a power of 19 mJ/cm². Keep gap between mask and sample chip to a minimum, with water in between.

8. Post-exposure bake at 90°C for 10 min and cool down in air.

9. Develop in SU-8 developer for 1 min, rinse with IPA, and nitrogen dry.

10. RIE in oxygen plasma for 4 min, at oxygen pressure of 160 mTorr (70%) and RF power of 80 to 83 W (27%).

Figure 2.6. Photo lithography process flow
2.1.2.3 Catalyst Patterning Using Electron-Beam Lithography

Another technique to create the catalyst pattern is e-beam lithography. In our lab, we use a Zeiss SUPRA55-VP FESEM system to do e-beam lithography (Figure 2.7).

![Figure 2.7. A picture of the Zeiss SUPRA55-VP FESEM system](image)

Scanning electron microscopes are used for a wide range of applications in material analysis, semiconductor industries, chemistry and biology. It uses a focused electron beam to scan the sample and produce images. A schematic of the components of an electron beam (given in yellow) is shown in Figure 2.8. Electrons are emitted by a gun, accelerated by a beam booster and focused by several lenses. The movement of the focused electron beam is controlled by scan coils. As shown in Figure 2.9, when the electron beam hits the sample surface, secondary electrons (SE) are created and detected by Inlens or SE2 detectors for imaging. Backscattered electrons (BSE) are also created during the interaction. Secondary electrons are generated by inelastic scattering of the electron beam on the atoms near the surface of a sample. On the
contrary, backscattered electrons are generated by elastic scattering in a much deeper range of the sample. Secondary electrons carry a lot of surface information that provides high image resolution, while the backscattered electrons are strongly related to the atomic number of the materials that can provide images with very good material contrast. In addition, X-rays can also be generated during the interaction that can be used to identify materials, details about this technique is given in Chapter 3.

Figure 2.8. A schematic of the SEM
Compared to traditional light microscopy, SEM has many advantages such as:

1. Much higher resolution
2. Large depth of focus
3. More control of magnification

Electron-beam lithography uses a focused electron beam and a beam-blanker to scan the sample surface covered with a layer of e-beam resist in a patterned fashion and thus transfer the designed patterns to the resist. The main advantage of e-beam lithography is that the resolution can reach nanometer regimes. Another advantage is that it does not require a mask.

In our e-beam lithography process, PMMA is used for catalyst patterning where openings in the PMMA define the areas where the catalyst will get deposited. Since PMMA is a positive photoresist, the areas that are exposed by the electron beam will become soluble in developer. The PMMA photoresist used here is PMMA 700, which is a custom mix I designed specifically
for the catalyst patterning step. It consists of PMMA 950 C10 (purchased from MicroChem Corp, Newton, MA) and chlorobenzene at a ratio of 2:1. This special formula is designed to provide a PMMA thickness of 700 nm.

In order to control the movement of the electron beam, a software package is used to communicate with the SEM. We use the commercial software Nano Pattern Generating System (NPGS) by JC Nabity Lithography Systems to carry out electron beam direct-write lithography. DesignCAD 2000 (part of the NPGS suite) is used to design the patterns. A typical catalyst pattern is shown schematically in Figure 2.10, with the red areas being the catalyst locations. The ‘L’ shaped patterns and the big square are the alignment marks, which are used to locate the coordinates of the selected carbon nanotubes. Once the pattern is designed, the pattern file is then integrated into a “Run File” (a specific file that is used in NPGS) that separates the exposure details from the pattern information. By modifying the run file, we can change the exposure conditions without changing the pattern design. Once the run file is generated, the NPGS program can read the run file and automatically write the designed patterns by controlling the scan coils and beam blanker of the SEM.

Figure 2.10. CAD design of the catalyst pattern using electron beam lithography
After the catalyst pattern is written, the sample is put into methyl isobutyl ketone (MIBK) developer (MIBK: IPA=1:3) for development. The parameters of e-beam lithography for catalyst patterning are given below:

1. Design catalyst pattern files (Figure 2.10).
2. Spin coat PMMA 700 at 4000 rpm for 45 sec;
3. Bake at 180 °C on hotplate for 2 min;
4. Expose the sample with an accelerating voltage of 30 kV with a dosage of 500 µC/cm²;
5. Develop in methyl isobutyl ketone (MIBK) developer for 80 sec, rinse with isopropanol, followed by nitrogen dry.

The accelerating voltage indicates the power of the electron beam. A small accelerating voltage (100 V-10 kV) is often used to map the surface of the sample while a large accelerating voltage (10 kV-30 kV) is often used for analytical and e-beam writing purposes. The dosage indicates the amount of time for which the electron beam is focused at one location on the sample. The larger the dosage, the longer the electron beam interacts with the certain area of the sample. Once the photoresist is patterned, the remaining steps are identical for both photolithography and e-beam lithography.

2.1.3 Catalyst Deposition

Before applying the catalyst suspension, it is first magnetic stirred for one hour using a magnetic stirrer. The catalyst is deposited by applying 3 droplets (≈50 µL) of the catalyst
suspension to the sample with a disposable dropper, resulting in complete coverage of the 7 mm × 10 mm sample surface. The sample is then allowed to sit on a flat surface to let the methanol in the catalyst solution to evaporate completely. A thin film is formed on the chip when dry. Then the chip is moved to a hotplate to bake at 85 °C for 3 min in order to promote catalyst adhesion to the SiO₂ surface.

After the chip has been allowed to cool in air, it is put into 10 ml of acetone for lift-off. Typically the lift-off takes less than 5 min and the un-needed catalyst layer on top of the un-exposed PMMA comes off as a whole piece. The chip is then removed from acetone, rinsed again with acetone following by isopropanol, and nitrogen dried. The whole process is illustrated in Figure 2.11.

![Diagram of the lithography process for catalyst deposition](image)

**Figure 2.11. Lithography process for catalyst deposition**
As shown in Figure 2.11, catalyst particles aggregate in the PMMA opening and pack firmly against the PMMA side wall and the substrate. As a result, the edges of the patterned catalyst islands are higher than the center. The height of the catalyst island is measured by atomic force microscopy (AFM). The result is shown in Figure 2.12. The height is measured at six points along the red line in the upper left image. The height difference between the two points with the same color is given as $|Z1-Z2|$ in the right table. The height at the edge of the catalyst island, which is the height difference between the two blue points, is measured to be about 400 nm. While the height of the center part of the catalyst island (red and green points) is around 200 nm.

Figure 2.12. AFM measurement of the height of the catalyst island; inset shows the positions of the catalyst island and the scan area
2.1.4 Comparison between Photolithography and E-beam Lithography

Both photolithography and e-beam lithography have been used in this research, although results indicate that e-beam lithography is more suitable. I find that catalyst islands created using e-beam lithography are better defined than those created using photolithography. This has been illustrated in Figure 2.13, where rectangular catalyst islands patterned using photolithography are small and irregular while those patterned using e-beam lithography are sharp and well-defined. It is very hard to optimize process parameters to reach the same level of quality for the catalyst islands using photolithography. Since these catalyst islands also serve as alignment marks for subsequent electrode patterning, it becomes very important that these catalyst islands start well-defined. Moreover, it is much easier to change catalyst patterns using e-beam lithography. Photolithography uses a mask to pattern the photoresist. When the feature of the pattern is small, the mask is usually made of glass with a metal pattern on it. A new mask is needed if any change of pattern is made. This is not the case with e-beam lithography. Without a predefined physical mask, e-beam lithography uses computer software to control the electron beam to expose the desired areas directly. Any changes can be easily made by modifying the pattern file on the computer. The main drawback of e-beam technology is low throughput, as it takes a long time for a fine nanometer scale electron beam to write a large area. However when doing lab research, this is not a big problem since high-volume manufacturing is not needed.
2.1.5 Carbon Nanotube Growth

A CVD method is used to grow carbon nanotubes in this research because of its simplicity, specificity in growth location, and high yield of SWCNTs. The furnace used is a three-zone high temperature furnace from Lindberg, type 59744-A. The three temperature zones are set to 750 °C, 900 °C and 750 °C respectively during carbon nanotube growth. Methane is used as the carbon feedstock due to its high kinetic stability at such high temperatures, which can decrease the thermochemical decomposition and the amount of amorphous carbon produced during the growth process [23]. Hydrogen is used to reduce the iron nitrate in the catalyst into metallic Fe. Hydrogen also serves to slow down the methane decomposition since hydrogen is a product of the decomposition of methane [25]. A schematic of the furnace set up is shown in Figure 2.14 and a photo of the setup is shown in Figure 2.15.
Figure 2.14. Schematic of the set up for CVD growth

Figure 2.15. A photo of the furnace with a close up of the quartz boat with samples; chip size: 7 mm × 10 mm
Sample chips are loaded into the quartz tube in a horizontal manner using a small quartz boat, which also serves to modulate the gas flow and reduce turbulence inside the tube. Generally, small quartz boats are used to produce laminar flow near the boat surface, providing long and straight CNTs [26]. The schematic of this design is shown in Figure 2.16.

![Diagram of flow and sample](image)

**Figure 2.16.** The use of a small quartz boat can reduce turbulence

Before turning the furnace on, the quartz tube is first sequentially purged with H$_2$, then CH$_4$, and finally Ar, and each purge lasts for 2 min. Then the three zones of the furnace are turned on to heat up to 750 °C, 900 °C and 750 °C respectively in a constant Ar flow. After the desired temperature has been reached, H$_2$ and CH$_4$ gases are turned on simultaneously and Ar is turned off to start the growth. The ratio of H$_2$ to CH$_4$ in the gas plays an important role in the outcome of the carbon nanotube growth. Since hydrogen is used to reduce the iron nitrate in the catalyst into metallic Fe, a larger supply of hydrogen generates a larger amount of Fe catalyst. As a result, more carbon nanotubes will grow from the catalyst islands, but the growth rate and final length of the carbon nanotubes are limited due to the relatively small supply of methane. For the contrary case, insufficient hydrogen generates a smaller amount of Fe catalyst, leading to less growth sites. In addition, excessive methane could cause amorphous carbon to form on the
catalyst islands, covering the surfaces of the catalyst and inhibiting carbon nanotube growth [23]. The experimentally optimized conditions for the gas supply ratio is at $\text{CH}_4 = 32$ sccm, and $\text{H}_2 = 27$ sccm. Growth time is typically 30 minutes to reach the desired carbon nanotube length. After growth, both $\text{CH}_4$ and $\text{H}_2$ are turned off, and Ar is turned back on during the cool down process, which usually takes about 4 hours. It is also noticed in our experiment that the introduction of Ar during the 30 minutes growth time influences the physical and electrical properties of in-plane carbon nanotube meshes. It is verified that the use of Ar influences the diameter distribution, as well as the field emission properties of the resulting carbon nanotubes by creating surface defects. Details about the influence of Ar on the growth of the CNTs are given in Appendix A.

2.1.6 Carbon Nanotube Imaging

The SEM is used to locate the catalyst islands and assess the quality of the synthesized carbon nanotubes. A small accelerating voltage (0.5 kV) is used for imaging because an electron beam with a large accelerating voltage could damage the carbon nanotubes.

As was shown in Figure 2.10, there are three groups of catalyst islands in each column. Only one group is chosen for each column since there is only one pair of source/drain electrodes for each column, as shown in Figure 2.18. The group of catalyst islands having straight and long CNTs is chosen to proceed onto the next steps of fabrication. Where one catalyst island out of five will be used as alignment mark. For example, the group in Figure 2.17(a) is chosen because it has one straight and long carbon nanotube while CNTs in the group in Figure 2.17(b) are short and curved. Straight CNTs are preferred since any curvature can strongly influence the electrical properties by creating defects on the CNTs. Long CNTs are also preferred since it is easier to
deposit metal contacts and protection layer (will be discussed later on) compared with short CNTs.

![Figure 2.17](image)

Figure 2.17. (a) Group of catalyst islands with one straight and long CNT (b) Group of catalyst islands with short and curved CNTs

### 2.2 Electrode Design and Deposition

E-beam lithography is used to pattern the photoresist and a sputtering system is used to deposit the metal.

To create the metal electrode pattern, a bilayer release process is used with e-beam lithography to create an undercut in the photoresist profile to facilitate lift off. Both methyl methacrylate (MMA) and poly(methyl-methacrylate) (PMMA 950 C2) are used. The thickness of the two resist layers are 500 nm and 100 nm, respectively. Similar to the process of patterning the catalyst islands, DesignCAD 2000 is used to design the electrode pattern, which is shown in Figure 2.18, with the black areas representing the catalyst pattern, and the blue being the electrode pattern. The acceleration voltage of the electrons for e-beam lithography is 30 kV. The area dosage is 350 µC/cm², which is lower than the dosage used for catalyst patterning since
MMA is more sensitive towards electron beam than PMMA (thus requires a lower dose). The aperture size is selected based on the pattern dimensions. For fine patterns with dimensions less than 1 µm, a 7.5 µm aperture is used while for patterns with dimensions of several hundred microns, a 120 µm aperture is appropriate. In this case, the widths of the electrodes are 1 µm to 2 µm, thereby a 30 µm aperture is used. While the big squares (pads to contact with probes) have a dimension of 400 µm, thereby a 120 µm aperture is used (Figure 2.18). After the exposure to electron beam, the samples are developed in Methyl isobutyl ketone (MIBK) developer for 70 sec. Note that PMMA has a higher molecular weight than MMA. In general, the higher the molecular weight, the lower the dissolution rate in a solvent developer. Therefore, an undercut forms during the development process because the MMA layer dissolves at a faster rate than PMMA. This undercut profile reduces any subsequent sidewall deposition of the metal, thus providing well-defined and clean metal structure. On the contrary, metal “ears” can be formed when only using PMMA layer. The metal “ears” are caused by metal along the sidewall standing upwards from the surface. A comparison of these two situations is illustrated in Figure 2.19. The undercut profile also promotes metal lift-off since the solvent can easily attack the photoresist through the undercut.
Figure 2.18. CAD design of the contact electrodes
Cr/Au is used for the electrodes, since Au has good contact with CNTs and high electrical conductivity, while the thin layer of Cr serves as an adhesion layer. The thickness of Cr and Au are 25 Å and 800 Å, respectively. SEM images of electron beam patterned devices are shown in Figure 2.20.

Figure 2.19. Comparison of vertical and undercut profiles in lift-off results
Left: Using only PMMA; Right: Using MMA/PMMA double layer
Red arrows indicate the solvent can easily attack the photoresist through the undercut, promoting metal lift-off
2.3 Electrical Characterization

An initial measurement of the CNT transfer characteristic is performed before any treatment of the CNT to determine whether the CNT is p-type semiconducting, ambipolar, or metallic. The measurement setup is illustrated in Figure 2.21.

Figure 2.20. SEM images of two CNTFET devices

Figure 2.21. Illustration of the setup for device characteristic measurements
A bias voltage of 20 mV is applied between source and drain electrodes. Part of the SiO$_2$ is removed by a diamond scribe to expose the Si back gate, albeit from the top surface. A sweeping gate voltage from -10 V to 10 V at steps of 0.2 V is applied to the silicon back gate and the resulting current passing through the source-drain circuit is monitored. A LabVIEW 2013 SP1 software program (National Instruments Corporation, Austin, TX) was implemented in an IEEE-488 environment, using a computer to control the Model 4140B pA meter/DC voltage source (Hewlett-Packard Inc., Palo Alto, CA, USA), and the CNTFET was connected to a four micromanipulators system to characterize device parameters.

Figure 2.22. Typical transfer characteristics for nanotube FETs, showing (a) semiconducting, (b) ambipolar, and (c) metallic behavior
Typical characteristic curves are shown in Figure 2.22, corresponding to three types of carbon nanotubes: p-type semiconducting, ambipolar (shows both p-type and n-type conductance), and metallic.

Figure 2.22(a) shows a typical p-type semiconducting CNT. This device is turned on and off due to the shift of the Fermi level resulting from the changes in gate voltage. As was shown in Figure 1.9, when a positive gate voltage is applied, the Fermi level can still lie within the band gap. Therefore there is no current flow and the device is off. When a negative gate voltage is applied, the Fermi level is brought into the valence band and the width of the Schottky barrier is small, enabling electrons to tunnel through the barrier. Therefore the device is turned on. When the negative gate voltage increases, the width of the Schottky barrier is decreased. Therefore an increasing of the source/drain current is observed (Figure 1.9(a)).

When the negative gate voltage keeps increasing, a saturation current is observed. The reason for the saturation current is that there is a maximum conductance in the carbon nanotube. The electron transport in CNTs can be considered as ballistic transport due to their quasi-1D structure. Ballistic transport is the electron transport with negligible resistance and is observed when the electron mean free path is large than the size of the transport media. In ballistic transport, there is a maximum conductance that only depends on the number of conduction channels. This maximum conductance is given by Landauer formula [20]:

\[
G = \frac{2e^2}{h} M
\]

where \( M \) is the number of conduction channels. Therefore, this maximum conductance saturates the current of the CNTFET at large negative gate voltages.
Figure 2.22(b) shows an ambipolar behavior. At negative gate voltages, the CNT shows a p-type conductance, which increases as the voltage goes more negative. However, at positive gate voltages, the CNT also shows an n-type conduction behavior, although lower than p-type conductance, as the current goes up with positive voltages. This indicates that the band gap of the CNT is small. When the band gap is small, the Fermi level can easily shift into the conduction band or valence band. Therefore, electrons can tunnel through the barrier at either positive or negative gate voltages. The band diagram of an ambipolar device is shown in Figure 2.23. The ambipolar behavior also indicates that the diameter of the CNT is large. Since the magnitude of the band gap for the carbon nanotubes is proportional to the inverse of the tube diameter [20], a large diameter leads to a small band gap.

![Band diagram of an ambipolar device](image)

Figure 2.23. Band diagram of an ambipolar device; since the Fermi level of the CNT lies closer to the valence band, the device shows more p-type conductance.
Figure 2.22(c) shows a typical metallic nanotube performance where the conductance is not dependent on the gate voltage. For CNTFET applications, either semiconductor or ambipolar devices are suitable.

Note that most of the devices fabricated show p-type conductance and in ambipolar devices, p-type conductance is dominant. This is mainly due to the hole-doping in CNTs by the oxygen molecules adsorbed on their surface. In addition, since Au has a high work function (5.1 eV), when the Fermi levels of Au and CNT lines up, the Fermi level of CNT is brought closer to the valence band. Therefore the device shows more p-type conductance [20].

In Figure 2.22, hysteresis is observed for the semiconducting devices and this is mainly due to charge trapping by water molecules [27]. The water molecules trap charges and screen the overall effect of the gate electromagnetic field generated by the gate and imparted on the carbon nanotube. The charge trapping water molecules exist either on the surface of the carbon nanotube or on the SiO$_2$ surface in close proximity to the carbon nanotube. This idea has been proven by many experiments such as measuring the CNTFET characteristics under vacuum (to remove the water molecules on or in the vicinity of the CNT surface), or measuring the characteristic of a suspended CNT (to remove SiO$_2$ surface bounded water molecules) [27]. Other causes include charge traps in bulk SiO$_2$ or at the SiO$_2$/Si interface, and oxygen-related defect trap sites near nanotubes resulting in hysteresis in CNT transfer characteristic. In order to further study the hysteresis effect seen in the electrical characteristics of CNTFETs, theoretical models are adapted. Details about the hysteresis modeling in CNTFETs will be given in Appendix B.
CHAPTER 3
TARGETED DEPOSITION OF GOLD NANOPARTICLES

In this chapter, the general utility of the gold nanoparticles, especially in sensor applications is introduced. Specific uses will be elaborated upon in subsequent chapters, while this chapter focuses on the deposition of gold nanoparticles onto CNTFET devices.

3.1 Gold Nanoparticle Introduction

Gold nanoparticles range in size from about a few nanometers to more than a hundred nanometers in diameter. Due to their small sizes, gold nanoparticles have very different properties compared to bulk gold. An SEM image of gold nanoparticles is given in Figure 3.1.

In general, nanoparticles have extremely large surface area to volume ratio, leading to applications such as catalysis and modification of the surface of the electrodes used in batteries [18]. Second, gold nanoparticles have very good electrical conductivity and because of this, they are often used as electron mediators, or electron shuttles, to help easily move electrons from one location to another. Gold nanoparticles also find use as conductors in next generation nano electronic chips, for interconnects between circuit elements like resistors, capacitors and inductors [28]. Third, gold nanoparticles possess interesting optical properties due to their small sizes. When gold nanoparticles interact with light having a wavelength much larger than the size of the gold nanoparticles, the electromagnetic field of the light can induce a resonant oscillation of the gold electrons on the surface of the gold nanoparticles [29]. This oscillation is also called surface plasmon resonance and leads to a strong enhancement of the particles’ ability to absorb
or scatter light. The frequency of the surface plasmon resonance can be tuned by changing the size of the gold nanoparticle, leading to tailored optical properties for different applications such as molecular labeling and biological imaging and detection [29]. In addition, gold nanoparticles have very good bio compatibility and offer unique surface chemical properties that includes the formation of strong covalent bonding between gold and any thiol groups found on biomolecules. This covalent bond provides a more robust bonding mechanism compared to nonspecific adsorption of biomolecules [30].

Figure 3.1. An SEM image of gold nanoparticles

With the unique properties discussed above, gold nanoparticles have been most widely used in biological and medical applications such as drug delivery, tissue engineering, protein and DNA sensing, diagnostics and bio-imaging [30]. In this investigation, Au nanoparticles are used to study the sensing mechanism of CNTFETs with GOx towards glucose. Details of the experiment will be given in Chapter 4. In addition, Au nanoparticle decorated CNTFETs are also
used to investigate the gas sensing mechanism of the CNTs. Details of these experiments will be given in the Chapter 5.

### 3.2 Electrodeposition of Au Nanoparticles

Previous work in our group has shown that Au nanoparticles can be deposited onto carbon nanotubes using electrodeposition [31]. A brief introduction of the in-situ Au nanoparticle electrodeposition method is given below.

First, a sacrificial Au electrode is included in the device design in close proximity to the CNTFET to serve as a source of Au, as shown in Figure 3.2. The sacrificial electrode is composed of a bilayer of metals Cr/Au, at 25 Å and 800 Å, respectively. It is located 20 μm away from the carbon nanotube.

![Figure 3.2. SEM image of the device configuration with a sacrificial electrode](image)

The setup used for electrodeposition of Au is illustrated in Figure 3.3. A drop (≈ 5 μL) of electrolyte phosphate buffered saline (PBS) is applied to the device, and a positive voltage is
applied to the sacrificial electrode, with both CNT contact electrodes grounded. Au atoms from the sacrificial electrode are oxidized by the positive potential and dissolve in the PBS as Au ions, and are reduced at the grounded electrodes and CNT side wall. An SEM image of the Au nanoparticles decorating a carbon nanotube is shown in Figure 3.4. Here the voltage applied on the sacrificial electrode is 1.5 V.

Figure 3.3. Setup for Au nanoparticle deposition
3.3 Site-Specific Deposition of Au nanoparticles

The process described above provides a way towards in-situ deposition of Au nanoparticles and can be easily expanded for batch fabrication. Since each device has its own sacrificial electrode, only the selected device will be decorated with Au nanoparticles. Further, if we deposit sacrificial electrodes using different metals for different devices, we will be able to deposit different metal nanoparticles onto different devices on the same chip. Because CNTFETs decorated with different metal nanoparticles have the potential to respond to different molecules, we can integrate CNT sensors onto one single chip and therefore greatly enhance the sensing efficiency.

In general, the process described above would lead to a random distribution of gold nanoparticles onto the carbon nanotubes and it would not allow for site-specific nanoparticle deposition on CNT devices. If it were possible to deposit Au nanoparticles onto preselected
locations on a CNT, it would allow the further investigation of the interaction between metal nanoparticles and the CNT, as well as the sensing mechanism of CNTFETs. In the next sections, a review of methods for site-specific deposition of Au nanoparticles onto CNTs from other research groups will be first discussed. After that, our site-specific deposition method will be given.

3.3.1 Other Methods for Site-Specific Nanoparticle Deposition

Velamakanni et al. has demonstrated a chemical approach to selectively deposit gold nanoparticles capped with the amino acid cysteine (Au-CysNP) onto the junctions of multiwalled carbon nanotubes networks to increase the electrical conductivity of the networks [32].

Cysteine has three functional groups: thiol (-SH), amino (-NH$_2$), and carboxylic acid (-COOH). The -SH group can interact with the gold nanoparticle via the strong gold-thiol bond, while the -NH$_2$ and -COOH groups can make chemical bonds with the complementary groups on functionalized carbon nanotubes. When one cysteine-capped gold nanoparticle is linked to a carbon nanotube chemically, the remaining groups on the same Au-CysNP can link to other carbon nanotubes. This results in a gold nanoparticle connecting two carbon nanotubes and trapping itself at the resulting intersection of the two carbon nanotubes [32]. TEM images showing Au nanoparticles at the intersections of carbon nanotubes are shown in Figure 3.5.
The experimental results obtained by Velamakanni et al. show that the electron transfer through CNT-Au nanoparticles junctions is higher than the electron transfer through CNT-CNT junctions. By specifically depositing Au nanoparticles onto the nodes of the carbon nanotube network, the electrical performance can be enhanced. This will lead to applications in transparent conductive films made with carbon nanotubes.

Another site-specific Au nanoparticle deposition method is through the use of an electrochemical dip-pen nanolithography method invented by Chu et al. [33]. This method uses an atomic force microscope to achieve site specific deposition. As shown in Figure 3.6, the tip of the AFM is first immersed in a gold chloride solution, and then a voltage is applied to the tip for the Au ions in the solution to reduce onto the CNT. As the tip sweeps over the carbon nanotube,
Au nanoparticles can be deposited onto the carbon nanotube through an electrochemical reaction. The result of an exemplary deposition sweep is shown in Figures 3.7.

![Schematic of electrochemical dip-pen nanolithography method](image)

**Figure 3.6.** Schematic of electrochemical dip-pen nanolithography method, adopted from [41]

However, the dip-pen nanolithography method is relatively inefficient since it only allows for deposition of the Au nanoparticles onto one site each time since the deposition occurs only when the AFM tip touches the carbon nanotube. Plus, the dip-pen nanolithography method does not provide for adequate Au nanoparticle number control due to the geometry of the AFM tip. As shown in Figure 3.7, the AFM tip was translated across the nanotube along the two dashed lines, resulting in two locations where Au nanoparticles attached to the CNT sidewall. However, at each location, there are two nanoparticles instead of one nanoparticle. Therefore, the number of Au nanoparticles each sweep could provide is not controllable.
Site-specific Au nanoparticle deposition can be accomplished using electrodeposition combined with e-beam lithography of a patterned PMMA layer. The electrodeposition process was described earlier in Section 3.4 (Figure 3.3).

In order to achieve site-specific deposition, a PMMA layer is first deposited and patterned to expose nanometer sized openings in the preselected locations for deposition. As shown in Figure 3.8 (a) and (b), a 100 nm thick PMMA layer (shown in green) is first spin coated onto the devices. Then e-beam lithography is used to open windows in the PMMA layer, specifically on the site along the CNT where the decoration is to occur and another exposing the area around the sacrificial electrode, allowing both regions to be exposed to the electrolyte, as shown in Figure 3.8 (c). Direct e-beam writing process is described in Chapter 2. The
accelerating voltage used in this process is 30 kV. The aperture size used is 30 µm and the dosage used is 350 µC/cm\(^2\). Once the openings are created, a drop of PBS is applied on the device and a voltage is applied to the sacrificial electrode, as shown in Figure 3.8 (d). In this way, the Au nanoparticles will be specifically deposited only within the preselected sites. A close up look of the PMMA opening on the carbon nanotube is shown in Figure 3.9.
Figure 3.8. SEM images of a CNTFET with sacrificial electrode (left) and its associated cross-sectional schematic diagram (right); (a) The as-fabricated device structure; (b) The device covered by a thin layer of PMMA (shown in green); (c) Openings created on the CNT and sacrificial electrode using e-beam lithography; (d) A drop of PBS is applied onto the device allowing the migration of Au ions to the CNT upon application of a voltage on the sacrificial electrode.
The width of the opening on the CNT channel is 100 nm. A voltage of 1.2 V is applied to the sacrificial electrode for 1 minute to provide a small number of Au nanoparticles on the CNT sidewall. As shown in Figure 3.9, a single Au nanoparticle is deposited onto the preselected location on the carbon nanotube. Here the optimized voltage and the deposition time are 1.2 V and 1 minute based on experiment. If the voltage is too small, there will be no Au nanoparticles nucleate on the CNT side wall. And if the voltage is too large, there will be a large Au cluster deposited on the CNT wall. The deposition time determines the size of the Au nanoparticle. Another SEM image of a single Au nanoparticle deposited on the carbon nanotube is shown in Figure 3.10 to show reproducibility of the process.
Figure 3.9. (a) CNT device covered with PMMA with an opening on the CNT (left) and a zoomed in schematic view of the opening (right); (b) one Au nanoparticle is deposited onto the CNT (c) An SEM image showing one single Au nanoparticle at the preselected location
By modifying the width of the PMMA opening, it is possible to deposit an array of Au nanoparticles. As shown in Figure 3.11, the width of the PMMA opening is set to be 3µm, and an array of Au nanoparticles on the CNT sidewall is obtained.
In addition, it is possible to create multiple PMMA openings and deposit Au nanoparticles onto those sites at the same time, as shown in Figure 3.12.
In order to verify that the nanoparticles are indeed gold, I conducted an energy dispersive X-ray spectroscopy (EDS) measurement on the nanoparticles. EDS measurements are often used to determine the elemental composition of a sample. When a high energy electron beam hits the
surface of a sample, an electron from the inner shell of the atom is excited to an outer shell, leaving a hole in the inner shell. Then an electron from the outer shell fills this hole and releases X-ray radiation. Since the energy of the X-rays are characteristic of the atomic structure of the element from which they were emitted, this allows the measurement of the elemental composition of the sample.

The EDS measurement results show that the nanoparticles obtained are indeed gold, as shown in Figure 3.13. The electron beam is first focused on the SiO$_2$ substrate, away from the carbon nanotubes and nanoparticles. The result shows the sample consists of Si and O, which is the elemental composition of the SiO$_2$ substrate. Then the electron beam is focused on the nanoparticle, with the result showing that the nanoparticle composition is gold and trace amount of C, which is often found on Au nanoparticles. The results confirm that the nanoparticles obtained are Au nanoparticles.
The size of the Au nanoparticles can be controlled by the length of the deposition time. Typically the size of the Au nanoparticles obtained is about 30nm – 60nm in diameter. An atomic force microscopy image showing the size of the Au nanoparticles is shown in Figure 3.14.

![Figure 3.13. EDS measurements probing (a) SiO$_2$ substrate and (b) one nanoparticle showing that the nanoparticle is a Au nanoparticle](image)
In order to control the size of the Au nanoparticles by the length of the deposition time, it is necessary to first apply a relatively high voltage to the sacrificial electrode for a short period of time. This allows the nucleation of Au nanoparticles on the CNT sidewalls. After that, a relatively low voltage is applied to the sacrificial electrode for a controlled time to increase the size of the Au nanoparticles already nucleated on the CNT sidewalls without creating new Au nanoparticles. Usually in the first part, the high voltage is set to 1.5 V for 2 seconds. In the second part, the low voltage is set to 1.2 V. The size of the deposited Au nanoparticles is about 30 nm in diameter for a deposition time of 40 seconds. For a deposition time of 60 seconds, the size of the Au nanoparticles is about 50 nm. For a deposition time of 90 seconds, the size of the Au nanoparticles is about 80 nm. And for a deposition time of 120 seconds, the size of the Au nanoparticles is about 55 nm.

Figure 3.14. AFM result showing (a) the AFM image of two Au nanoparticles; (b) the three dimension image of the two Au nanoparticles and; (c) the result showing the size of the Au nanoparticles are about 55nm.
nanoparticles is 100 nm to 150 nm. The sizes of the Au nanoparticles obtained range from 10 nm to 150 nm. The relation between the particle sizes and deposition time that is obtained from one experiment is given in Figure 3.15. The SEM images of Au nanoparticles of different sizes are shown in Figure 3.16. Future experiments are needed to exam the reproducibility of the relation between nanoparticle sizes and deposition time.

<table>
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<th>Deposition time (s)</th>
<th>40</th>
<th>60</th>
<th>90</th>
<th>120</th>
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<tbody>
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<td>Nanoparticle size (nm)</td>
<td>30.36</td>
<td>47.17</td>
<td>81.47</td>
<td>150.30</td>
</tr>
</tbody>
</table>

Figure 3.15. A table (a) and a graph (b) showing the relation between the Au nanoparticle size and the deposition time.
3.3.3 Specific Deposition of Au Nanoparticles Using Joule Heating of CNTs

A simpler, albeit restrictive alternative to using e-beam lithography to open the window on the PMMA layer, is to use Joule heating of the carbon nanotubes. Joule heating occurs when electrons collide with atoms, generating heat locally. This heat is sufficient to melt a thin PMMA layer over the CNT, creating a small opening for Au nanoparticle deposition. Controlled experiments have been conducted by operating CNTFETs under different voltage biases. As the
voltage bias across the carbon nanotube increases, more heat was generated. The detailed process is as follows.

First, PMMA 950 C2 is diluted in chlorobenzene at a ratio of 1:2 to form a new consistency of PMMA. This new PMMA is spin coated onto CNTFET chips, providing a thickness of 40 nm at a spin rate of 4000 rpm. I measure the transfer characteristic of the CNTFET and select a gate voltage corresponding to an ON-state saturation source/drain current. Then I fix the gate voltage at this value to keep the device at ON-state, and gradually increase the source/drain voltage. With the source/drain voltage increasing, the current through the carbon nanotube increases. Therefore the heat generated also increases. It has been shown that the temperature of CNT can be raised to around 600 °C by such Joule heating [34], while the melting point of PMMA is only at 140 °C. When enough heat is generated by the carbon nanotube, an opening is created. An SEM image is shown in Figure 3.17.

Figure 3.17. An opening of PMMA created by Joule heating, the entire surface is covered by a thin layer of PMMA. Insert shows a close up image of the opening
As shown in the larger figure of Figure 3.17, we can see the color of the carbon nanotube is not uniform. The dark portion of the carbon nanotube is covered by a thin PMMA layer and the white portion of the carbon nanotube is exposed. As shown in the insert, only part of the carbon nanotube channel is exposed, which indicates that the generated heat is not uniform throughout the carbon nanotube. It has been shown by other groups that if the power dissipation through the CNT is uniform, the highest temperature occurs in the middle of the tube. Otherwise, the highest temperature occurs at the defect sites [34] since the heat generated is proportional to the square of the current multiplied by the resistance as shown in equation (5), and the resistance is largest at defect sites.

\[ Q \propto I^2 \cdot R \]  \hspace{1cm} (5)

It is also interesting to note that the carbon nanotube in Figure 3.17 is broken at the exposed part. This is caused by the oxidation of the CNT. Under high temperature, the C-C bond is broken due to desorption of CO in the presence of oxygen, leading to the degradation of the CNT [35]. This proves that the generated heat does open a small window on the thin PMMA layer and expose the CNT to oxygen.

In order to experimentally verify this, I tried to deposit Au nanoparticle onto the carbon nanotubes. As is shown in Figure 3.18, Au nanoparticles are deposited only onto the white portion of the carbon nanotube. Thus it can be conclude that the white portion of the carbon nanotube is exposed due to Joule heating.

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The results show that this method can be used to create sites for nanoparticle deposition. Moreover, the opening is very small (about the size of a CNT), enabling specific deposition of Au nanoparticles. It is also noticed that the PMMA opening is usually around 1 \( \mu \text{m} \) long. I assume that when the length of the carbon nanotube channel is reduced to about 1 \( \mu \text{m} \), the heat generated would be relatively uniform through the carbon nanotube, enabling the control of the heating sites, which may lead to possible applications of carbon nanotubes as nano scale heaters.

Figure 3.18. (a) (c) SEM images showing the small PMMA opening on top of the CNT; (b) (d) Au nanoparticles deposited only onto the exposed portion
3.4 **Decoration of Carbon Nanotubes with Other Metal Nanoparticles**

Aside from decorating CNTFETs with Au nanoparticles, I also tried decorating CNTFETs with Pd and Pt. Previous work has shown that Pd or Pt nanoparticle decorated carbon nanotubes have wide applications including non-enzymatic glucose sensing \[36, 37\], and gas sensing \[38\]. Experiments have been conducted to explore if Pd/Pt decorated CNTFETs can have similar applications, and to understand the functionalization of CNTFETs with Pd/Pt decoration.

### 3.4.1 Pd Nanoparticle Decoration

The process for Au nanoparticle deposition is adopted to deposit Pd onto carbon nanotubes. Perchloric acid (HClO₄) is used as the electrolyte since Pd can be dissolved in it. A voltage of 2V is applied to the sacrificial Pd electrode. The Pd sacrificial electrode is successfully dissolved in perchloric acid. However, I was not able to reduce Pd ions onto the CNT side wall. In future research, we will try to find the reduction potential of Pd ions and reduce Pd ions onto carbon nanotubes.

### 3.4.2 Pt Nanoparticle Decoration

Pt nanoparticles have been deposited onto CNTFETs using cyclic voltammetry (CV) method with the help of Dr. Dejun Chen in Professor Tong’s group. Cyclic voltammetry is an electrochemical technique which measures the current that develops in an electrochemical cell by cycling the potential of a working electrode \[39\]. In this experiment, the working electrode is connected to one of the S/D electrodes, leaving the other S/D electrode unconnected. The voltammetry cell contains 0.1 M HClO₄ and H₂PtCl₆. The voltage applied on the working
electrode sweeps from -0.3 V to 0.8 V at a rate of 50 mV/s. Pt ions in the solution are then reduced onto the CNT side wall under the influence of the potential applied on the working electrode. This voltage is swept for 7 cycles. An SEM image showing the deposited Pt nanoparticles is shown in Figure 3.19.

As is shown in the image, one electrode is deposited with Pt nanoparticles while the other electrode is not. This phenomenon is due to the potential drop across the CNT. The resistance of the CNT is relatively high and the potential drop across the CNT is large. Therefore there is not enough potential applied on the other electrode sufficient to reduce the Pt ions. A schematic diagram of this phenomenon is shown in Figure 3.20.

Further experiments will be carried out to investigate the possible application of non-enzymatic glucose sensors using Pt decorated CNTFETs.
3.5 Interaction between Au nanoparticles and CNTFETs

A fabricated CNTFET device is first characterized for its $I_{SD}$ versus $V_G$ behavior prior to Au decoration which is compared with the electrical behavior after the Au nanoparticles have been deposited using the process described earlier in this chapter. A change in the transfer curves of the CNTFET after the Au nanoparticle decoration is observed, that is the saturation current of the CNTFET has increased, as shown in Figure 3.21.

Figure 3.20. A schematic diagram showing the potential drop across the CNT. There is sufficient potential on the S/D electrode connected to the working electrode while there is insufficient potential on the S/D electrode close to the counter electrode to reduce the Pt ions.
As discussed in Chapter 2, when a metal and a semiconducting CNT are placed in contact, Fermi level alignment occurs resulting in a charge redistribution and the formation of a Schottky barrier. When a Au nanoparticle is deposited onto a semiconducting CNT, it will also experience this effect and create a local Schottky barrier on the CNT side wall. Intuitively, it would seem that these Schottky barriers should act as electron scattering sites and thus decrease the saturation current. However, this contradicts the findings from experimental results. This was quite puzzling and prompted discussions with a theoretician who studies CNT phenomena [Professor Ghosh from University of Virginia]. He suggested that one possible explanation for this increase in saturation current, or equivalently, the saturation conductance, is an increase of the transmission modes due to electron scattering. When electrons enter the Au
nanoparticles through the Schottky barriers, they lose energy due to the excitation of phonons, creating new transmission modes. It has been shown that the conductance, \( G \), depends on the average transmission per mode multiplied by the number of modes \([20] \), as shown in Equation \((6)\), where \( e \) is the elementary charge, \( h \) is the Planck constant, \( M \) is the number of modes, and \( T \) is the transmission per mode. Although scattering reduces the average transmission per mode, the current can still increase due to the increased number of modes.

\[
G = \frac{2e^2}{h} MT \tag{6}
\]

However, after a bit more thought, a more possible cause for the increase in saturation current is the effect of device processing. As described earlier in chapter, the fabrication steps for Au nanoparticle deposition involves the use of both photoresist (PMMA) and an electrolyte buffer (PBS). These processes may leave residue on both the Au electrodes and on the carbon nanotubes, changing the work function of the electrodes as well as the gate capacitance of the CNT, leading to a change in the CNTFET’s conductance.

To alleviate changes in the electrical characterization due to processing, a recovery process for the CNTFETS is used after each step during the fabrication and deposition process. The idea is to use high vacuum and high temperature to remove as much residue as possible on the carbon nanotubes. The devices are placed in a glass flask, which is then placed in a sand bath for uniform heating. The temperature in the flask is thus controlled by a hotplate. The flask is sealed using a rubber stopper and connected to a mechanical vacuum pump. A schematic and a picture of the recovery process set up is shown in Figure 3.22.
The temperature in the flask is set to 200 °C and the recovery process lasts for 20 minutes. As illustrated in Figure 3.23, before the recovery process, the saturation current of the CNTFET shows an increase after the PMMA deposition and removal process. After the recovery process, the saturation current decreases and the transfer characteristic curve is almost the same as that before the PMMA deposition and removal process. These results show that even the simplest of deposition and removal processes have an effect on the transfer characteristic of the CNTFETs, but by using a recovery process, this effect is effectively mitigated. Therefore, by using a recovery process after the complete Au nanoparticle deposition process, the interaction between Au nanoparticles and CNTFET can be more accurately investigated.
After incorporating the recovery process to the subsequent experiments on a newly fabricated device, I found that the saturation current of the CNTFETs actually decreases after Au nanoparticle deposition as was expected. As shown in Figure 3.24, immediately after the Au nanoparticle deposition, the saturation current of the CNTFET increases while after the recovery process, the saturation current decreases and is lower than the original curve. This result matches...
the theory of the creation of a local Schottky barrier on the CNT side wall, upon deposition of a Au nanoparticle, which acts as an electron scattering site to decrease the saturation current.

In order to further study the interaction between Au nanoparticles and CNTFETs, Au nanoparticles are deposited onto CNTFET one by one using the site-specific deposition method described earlier in chapter. Note that each individual nanoparticle deposition requires a blanked PMMA coverage, e-beam lithography to open each individual location where the Au nanoparticle should be deposited, then removal of the PMMA layer. Thus, after each deposition, a recovery process was imperative to eliminate the effects of the processing. The results show that the conductance decreases systematically as the number of Au nanoparticles on the CNT side wall increases, as shown in Figure 3.25.
Figure 3.25. (a) Transfer characteristic of a CNTFET, and SEM image showing the CNTFET without Au nanoparticles; (b) The conductance decreases after the first deposition (shown in red curve), where the SEM image shows one Au nanoparticle deposited on the CNT side wall; (c) The conductance further decreases after the second deposition (shown in blue curve), and the SEM image shows a second Au nanoparticle deposited on the CNT side wall.
Another property of the interaction between a Au nanoparticle and a carbon nanotube is that it appears to be size dependent. When the size of the Au nanoparticles is small, the height of the Schottky barrier is less than that of bulk Au [40], and the Schottky barrier height increases with the increasing size of the nanoparticles. However when the size of the nanoparticles becomes larger than approximately 20 nm in diameter, the potential barrier between the nanoparticle/carbon nanotube interface is no longer size dependent [41]. In effect, the nanoparticle acquires bulk properties and the potential barriers act as scattering sites to decrease the charge mobility. When the CNT is covered with a continuous coating of Au nanoparticles, the decreased conduction may also occur due to a screening effect on the gate voltage [42, 43].
CHAPTER 4
DIABETES, AND AU NANOPARTICLES ON CNTFETS FOR GLUCOSE SENSING

In this chapter, details of the functionalization procedure of CNTFETs for glucose sensing will be given. A background on diabetes and glucose sensing will be introduced at the beginning. Followed by details of the design, fabrication, and functionalization of the CNTFETs using Au nanoparticles for glucose sensing. The functionalization of the CNTFETs makes the sensing of the CNT devices selective towards glucose. Plus, it can potentially increase the sensitivity of the CNT sensors. The functionalization procedure involves the Au nanoparticle deposition on the CNT and glucose oxidase (GOx) incubation.

4.1 Diabetes Facts

Glucose sensors are mostly used in the management of diabetes. However, our group has developed them for first-responder critical care to evaluate blood volume loss, which is directly correlated to glucose concentration. Diabetes, also known as diabetes mellitus, is a group of metabolic diseases characterized by high levels of glucose in the blood. In the human body, glucose concentrations need to be regulated within a certain range, and this is accomplished by insulin, a hormone that removes excess glucose from the blood. There are three main types of diabetes: In type 1 diabetes, the body does not produce insulin, which can occur at any age. It is most often diagnosed in children, adolescents, or young adults. In type 2 diabetes, either the body fails to use insulin properly or the body does not produce enough insulin. Type 2 diabetes is
the most common form of diabetes and is often called adult-onset diabetes, where the body becomes predisposed to insulin-resistance. The last main type of diabetes is gestational diabetes, which is a condition when women previously without diabetes, have a high blood glucose level during pregnancy, leading to the development of type 2 diabetes. People with diabetes experience blood glucose highs (hyperglycemia) and lows (hypoglycemia), which may lead to both chronic and acute health problems. Diabetes raises the rates of stroke and heart disease death 2 to 4 times higher than normal. Diabetes is also the leading cause of microvascular complications such as kidney failure, blindness among adults, and lower-limb amputations [44]. Hyperglycemia can be toxic, however, it is the hypoglycemic condition that is most troublesome for persons with diabetes. Hypoglycemia can cause an inadequate supply of glucose to the brain, resulting in seizures, unconsciousness, permanent brain damage and even death.

The World Health Organization [45] estimates that currently more than 346 million people worldwide have diabetes and this number is predicted to more than double by 2030 without intervention. In the United States, about 25.8 million children and adults (8.3% of the population) have diabetes. More than 200,000 people die each year from a diabetes-related complication, making it the seventh leading cause of death in United States [45]. Therefore, early diagnosis, management, and care of diabetes is crucial for people afflicted with the disease.

4.2 Glucose Sensors Based on CNT

Glucose detection plays a key role in the management of diabetes. To date, many technologies have been pursued to develop new types of glucose sensors [46]. Among them, carbon nanotubes, due to their remarkable mechanical, electrical, thermal and chemical
properties, have been intensively investigated as sensing element of various glucose sensors. For example, Lin et al. has connected vertically aligned carbon nanotube bundles to a metallic electrode to measure the current response upon exposure to glucose solution [47]. Glucose oxidase was covalently immobilized on CNT nanoelectrode ensembles. The detection of glucose was realized by sensing the change in hydrogen peroxide liberated from the reaction between glucose oxidase and glucose. Guiseppi et al. has attached carbon nanotubes onto a carbon electrode surface, and realized electrochemical detection of glucose with cyclic voltammograms (CV) [48]. Glucose oxidase was adsorbed onto carbon nanotube bundles. Electrons generated through the interaction between glucose oxidase and glucose were directly sensed by the carbon nanotube and the carbon electrode. Similarly, Kuang has used a Pt nanoparticle modified carbon nanotube electrode grown directly on a graphite substrate to monitor the current response upon exposure to glucose [49]. In addition to these applications, where carbon nanotubes are mostly used to modify the electrode surface owing to their high surface to volume ratio, P. W. Barone and M. S. Strano have used the optical properties of single walled CNT for glucose detection [50]. Dextran coated CNTs will aggregate when concanavalin A is added to the CNT solution, decreasing the fluorescence of the CNTs. The introduction of glucose can cause the dissolution of CNT aggregation, leading to fluorescence recovery. Charlie Johnson’s group has used boronic acid functionalized carbon nanotube field effect transistors to detect glucose [51]. Glucose concentration is detected by monitoring the source-drain current of the device, which decreases due to the increased carrier scattering caused by the presence of boronate anions formed when glucose binds to the boronic acid receptor. In this research work, carbon nanotube field effect
transistors functionalized with Au nanoparticles and glucose oxidase are studied as the glucose sensing element.

### 4.3 Glucose Oxidase

Glucose oxidase, or GOx, is an enzyme that catalyzes the oxidation of glucose to D-gluconolactone. Glucose oxidase is the most widely used enzyme in the field of biosensors [52], especially for the detection of glucose in body fluids, owing to a relatively high selectivity, sensitivity and stability. The key component of GOx is the oxidation-reduction (redox) center called flavin adenine dinucleotide (FAD). A schematic diagram of GOx with FAD is shown in Figure 5.1. FAD is a component in biological redox reactions, which involve a gain or loss of electrons from a molecule. On interaction with glucose, FAD is reduced to FADH$_2$ (hydroquinone form), by accepting two hydrogen atoms (a net gain of two electrons), whereas glucose loses two hydrogen atoms and forms the redox product, gluconolactone. The chemical reduction reaction can be expressed as follows [53]:

\[
\text{GOx(FAD) } + \text{ glucose } \rightarrow \text{ GOx(FADH}_2\text{) } + \text{ gluconolactone}
\]  

Or

\[
\text{GOx(FAD) } + \text{ GOx(FADH}_2\text{) } \rightarrow \text{ GOx(FADH}_3\text{) } + \text{ gluconolactone}
\]
In the presence of oxygen, the reduced GOx(FADH$_2$) can be regenerated to GOx(FAD). That is, the reduced form of GOx can be quickly oxidized, yielding a by-product of hydrogen peroxide (H$_2$O$_2$). The chemical oxidation reaction can be expressed as follows:

\[
\text{GOx(FADH$_2$) + O}_2 \rightarrow \text{GOx(FAD) + H}_2\text{O}_2
\]  

(9)

FAD redox active center is physically embedded with the enzyme core and is protected by a thick protein pocket (Figure 4.1), so the electron transfer between GOx and the electrodes is not readily accomplished and becomes limited. The structure of glucose oxidase implies it is orientation-specific such that for the electron to be detected, it must be able to reach the electrode through the opening of the pocket, as illustrated in Figure 4.2. When glucose is able to bind with the FAD, the detection of glucose becomes possible, and is commonly achieved through the detection of H$_2$O$_2$ (First generation enzymatic glucose sensor). The generated H$_2$O$_2$ is monitored amperometrically since it can be oxidized to oxygen at a voltage of 0.7 V versus saturated calomel electrode, as illustrated in the chemical reaction equation below (Equation (10)). Since oxygen is naturally dissolved in aqueous solutions and present in human blood, the generated oxidation current of H$_2$O$_2$ can be measured, from which the concentration of glucose in the sample can be determined [54].

\[
\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-
\]  

(10)

The main problem with this method is that the voltage at which hydrogen peroxide is oxidized coincides with the oxidation potential of numerous other compounds found in blood,
such as uric acid, ascorbic acid and bilirubin, which can interfere with the detection of the target glucose [55]. These interferents can lead to either false positives or false negatives of a hypo- or hyper-glycemic condition.

Figure 4.1. A schematic of GOx, formed with the FAD in the core and a carbohydrate shell out side. Adapted from [56]

Figure 4.2. Effect of the GOx orientation on the electron transfer. Adapted from [57]
Mediators are often utilized in place of oxygen as electron acceptors (Second generation enzymatic glucose sensor). Mediators are small redox active molecules that have the ability to diffuse everywhere, including the protein pocket that wraps around the GOx, and can react with FAD, and diffuse out and react with the electrodes, shuttling the electrons between GOx and electrodes [58]. Mediators ideally react with GOx at a considerably faster rate than oxygen. They also have a suitably lower redox potential than H$_2$O$_2$ to avoid oxidation of interferents.

Researchers have found ferrocene and its derivatives to be efficient electron acceptors for glucose oxidase [59]. Potassium ferricyanide as a mediator has also been studied and used in commercial glucose sensors [60]. Other mediators such as quinones [61], transition-metal complexes [62] and similar compounds have also been used.

There are still problems when using mediators. Specifically, they are difficult to hold in place and in proximity to both electrodes and enzyme since these mediators are often small and diffusive.

Enzymatic glucose sensors based on direct electron transfer (Third generation enzymatic glucose sensor) have been developed to overcome the problems of glucose sensors using mediators. In direct electron transfer, the electrons directly transfer between electrodes and enzyme molecules. This kind of sensor provides less interfering actions and fast electron transfer rate due to the absence of mediators. One approach towards direct electron transfer is to reduce the distance between the redox active center and the electrodes (refer to Figure 4.2). In recent years, many research activities have been devoted to the development of nano-sized and porous electrode material that enables more efficient and direct electron transfer between enzyme and electrodes. Such mesoporous materials have been used to modify electrodes, creating a large
surface area that is able to entrap the enzyme [63], thereby shortening the diffusion distance from the redox centers of the enzyme to the electrode.

Other than mesoporous materials, carbon nanotubes [64, 65] have shown great promise for direct electron transfer. The similarity of sizes between carbon nanotubes and enzymes makes them favorable for biosensors. The large surface area and the nanostructure topology allow the enzyme to be adsorbed and shorten the distance to the redox center. Some carbon nanotubes may even ‘pierce’ the protein shell of GOx and reach within tunneling distance of the redox center [56].

4.4 Au Nanoparticles

Au nanoparticles is another kind of nano material that has been used to enhance the electron transfer between enzymes and electrodes. Studies have shown that electrodes containing Au nanoparticles have a much higher sensitivity to the enzymatic activity of GOx than those without Au nanoparticles [66, 67]. Au nanoparticles with appropriate dimensions (less than 30 nm) can ‘shuttle’ electrons from the redox active center to the electrodes. Some possible mechanisms behind this phenomenon have been proposed. First, the large surface area to volume ratio of the small Au nanoparticles greatly enhances the enzyme adsorption ability compared to the flat surface of the electrodes. Second, Au nanoparticles can reorient the GOx molecules to a preferable direction when they are adsorbed onto Au nanoparticles [68, 69], shortening the distance of which electrons travel. A GOx molecule comprises a hydrophilic FAD in the core of the molecule wrapped by a hydrophobic shell out side [68], as shown in Figure 4.1. This shell is flexible and deformable. When GOx adsorption onto an Au nanoparticle occurs, the amphiphilic
GOx molecule deforms to enable attachment to the hydrophilic Au nanoparticle surface through its hydrophilic FAD [70], thereby shortening the distance between FAD and Au nanoparticles. A schematic of the adsorption is shown in Figure 4.3 (a), where the adsorption of GOx onto a Au nanoparticle is illustrated through the attachment of its hydrophilic FAD to the hydrophilic Au surface. In contrast, Figure 4.3 (b) shows the adsorption of GOx onto a hydrophobic SiO$_2$ nanoparticle, where attachment of its hydrophobic shell to the hydrophobic SiO$_2$ surface is favored. Another possible mechanism is the quantum size effect of the Au nanoparticles, where some important properties of the particles including electronic properties and redox potential are altered when the particle size is reduced to nanoscale. When the number of atoms in a nanoparticle decreases, the redox potential tend to increase and thus, leads to a stronger affinity to electrons [67], making the electron transfer between the enzyme and electrodes greatly enhanced.

---

Figure 4.3. Schematic diagrams of different GOx adsorption onto (a) Au (b) SiO$_2$
Adapted from [70]
4.5 Functionalization of CNTFETs in Aqueous Environment

CNTFETs are prepared following the process described in Chapter 2. Functionalization of the CNT with GOx is done in an aqueous environment, as is the detection of glucose after GOx deposition. Therefore CNT-based transistors are required to function in liquid environments. However, degradation of CNTFETs occurs when the devices are in solutions and are biased to be in the ON-state.

For example, a droplet (≈ 5 µL) of glucose solution is applied on top of the CNTFET. The source/drain voltage of the CNTFET is fixed to 20 mV, and the gate voltage is sweeping form -10 V to 10 V. The exposure to aqueous media degrades the CNTFETs instantly during the I-V\_G characteristic measurement. Some CNTFETs were damaged (CNT is open-circuited) immediately after exposure to the glucose solution, as shown in the I-V\_G characteristics of Figure 4.4 (a). Other devices show inconsistent current values, specifically a very high source/drain current (two magnitudes larger than normal saturation current) when in glucose solution (Figure 4.4 (b)) and furthermore, the current in the CNT is greatly lowered after the glucose solution is rinsed away in DI water and the chip is dried. This is shown in Figure 4.4 (c), where the blue curve is the transfer characteristic before the exposure to glucose solution, while the red curve represent the transfer characteristic after the chip has been rinsed and dried.
This experiment was also repeated with PBS and DI water successively in place of the glucose solution. The same results are obtained, indicating that it is the aqueous media that degrades the CNTFET devices.

Another phenomenon to notice is that the high source/drain current always occurs for the ON-state and there is no current for the OFF-state, as shown in Figure 4.5. This is important
because if this current is a result of leakage through the path formed by liquid, it should not have any gate dependency. The reason for the degradation is still unclear. One possible explanation is that the liquid at the CNT/electrode junction can change the property of the contact interface, and greatly reduce the contact resistance. In addition, the gate voltage also affects the potential of the liquid, and the potential applied to the Au electrodes. When this potential reaches the oxidation potential of the Au, it degrades and is dissolved in the liquid.

Figure 4.5. Two devices showing that high source/drain current occurs only at ON-state

4.6 SU-8 Passivation Layer

In order for the CNTFETs to function properly in aqueous environment, protection layer is used to cover both source and drain electrodes. PMMA was first used as protection layer. Most of the CNTFET is covered by PMMA, only leaving the middle section of the carbon nanotube channel exposed to the solution. During the measurement, degradation of the carbon nanotube still occurs, indicating that liquids can ultimately permeate through the PMMA protection layer. An alternative is to use SU-8 to cover the source/drain electrodes. SU-8: 2002 is purchased from
MicroChem Corp. Newton, MA. An SEM image of the SU-8 passivation, or protection layer, is shown in Figure 4.6.

![SEM image of SU-8 protection layer](image)

Figure 4.6. (a) A CNTFET (b) Same device with SU-8 protection layer completely covering the electrodes (Au electrodes cannot be seen)

The protection layer is patterned using e-beam lithography, which is normally used for PMMA direct-write resists, but can be used with the negative SU-8 photoresist. The SU-8: 2002 is first spin coated onto the sample at a spinning speed of 2000 rpm for 30 seconds, forming a 2.5 µm thick film. Following the manufacturer specified protocol, the sample is baked at 95 ºC for 1.5 minutes to evaporate the solvent and densify the film. The SU-8 film is then exposed to the electron beam for patterning and is followed by a bake at 95 ºC for 2.5 minutes immediately after exposure in order to selectively cross-link the exposed portions of the film. Since SU-8 is very sensitive to an electron beam, the aperture used during the e-beam writing process is 7.5 µm instead of 30 µm and 120 µm normally used for electrode patterning. In addition, the beam current dosage is also kept at the minimum value of 1 µC/cm². Being a negative photoresist, the
SU-8 will remain on the substrate when exposed to the electron beam. Therefore, the pattern for the protection layer is almost the same as the pattern for the electrodes themselves. The difference is that the protection layer is designed to be longer than the electrodes, as was shown in Figure 4.6. The reason for this is that the electron beam always stays a little bit longer at the end of the pattern, which is the tip of the electrode pattern in our design. If the tip of the protection layer is too close to the CNT channel, the SU-8 may cover the CNT channel due to over exposure, as illustrated in Figure 4.7. Finally, the chip is immersed in SU-8 developer for 1 minute to remove the unexposed portions of the film. SU-8 is very easily exposed by electron beam, even with the smallest aperture and the lowest dosage of current, as described earlier. Therefore, the alignment and width of the SU-8 protection layer should be very precise. Otherwise, the SU-8 layer may not cover the electrodes completely, as shown in Figure 4.8(a), or the carbon nanotube channel would also remain covered, as shown in Figure 4.8(b). In addition, the SU-8 layer should be about 1 µm wider than the Au electrodes so that the liquid cannot easily permeate the side walls of the SU-8 protection layer.
Figure 4.7. (a) A schematic of the CNTFET; (b) The CNT channel is covered by SU-8 when the SU-8 passivation layer uses the same pattern as that of the S/D electrodes; (c) The CNT channel is exposed when the SU-8 passivation layer pattern is longer than the S/D electrodes pattern

Figure 4.8. (a) SU-8 passivation misses the electrodes; (b) CNT is covered by SU-8
In order to further confine the liquid, a second passivation process using SU-8: 2025 is employed, which provides a thicker passivation layer (25 µm). This process uses photolithography instead of e-beam lithography to cover most of the sample, exposing only the area close the CNTs. SU-8: 2025 is first spin coated onto the sample at 4000 rpm for 30 seconds to create an SU-8 film that is 25 µm thick. Following the manufacturer specific protocol, the sample is pre-exposure baked at 65 ºC for 30 seconds and 95 ºC for 1.5 minutes to evaporate the solvent and densify the film. The SU-8 film is then exposed to the UV light for 13 seconds for patterning. The sample is then baked at 65 ºC for 1 minute and at 95 ºC for 5 minutes after exposure to selectively cross-link the exposed portions of the film. Finally the chip is immersed in SU-8 developer for 4 minutes to remove the unexposed (and therefore, un-crosslinked) portions of the film. Figure 4.9 shows optical microscope images of the SU-8 passivation layer.
After the passivation process, the CNTFET devices can function properly in aqueous environments since the metal electrodes are all covered. The transfer characteristic curves for a CNTFET in air and subsequently immersed in PBS is shown in Figure 4.10. A significant change in the hysteresis is evident and a slight increase in the saturation current is observed when the device is in PBS.

Figure 4.9. Optical microscope images showing the devices protected by the SU-8 passivation layer. The blue area is the exposed SU-8 channel where the CNTs will be exposed to glucose solution. The light brown area is the SU-8 passivation layer. The insert shows a zoomed in image of the Au electrodes covered by SU-8.
The increased hysteresis is a result of the increase in the number of water molecules on and around the carbon nanotubes. When the number of water molecules around the carbon nanotube increases, the corresponding charge trapped by water molecules also increases, thereby increasing the hysteresis width.

The transport characteristics also exhibit an increase in saturation current, along with the hysteresis change, and may be caused by the change in gate coupling strength when in the presence of water. For a single walled CNT, its total resistance $R$, is the sum of three contributions,

$$R = \frac{h}{4e^2} + R_c + R_t$$  \hspace{2cm} (11)
where \( \frac{h}{4e^2} \) is the quantized contact resistance for a 1D system [71]. \( R_c \) represents an extra contact resistance due to imperfect contacts, and \( R_t \) is the resistance arising from the presence of scattering sites. This resistance has a corresponding conductance, \( G_t = 1/R_t = Q/(tV_t) \), where \( Q \) is the amount of charge flowing through the CNT, \( t \) is the transit time, and \( V_t \) is the potential difference in the CNT. More specifically, \( Q = C_c|V_g - V_{th}| \) where \( C_c \) is the capacitance per unit length of the CNT, \( V_g \) is the gate voltage and \( V_{th} \) is the threshold gate voltage, and \( t = L/v = L/\mu V_t \), where \( L \) is the nanotube length, \( v \) is the carrier drift velocity, and \( \mu \) is the carrier mobility. Therefore, the intrinsic tube conductance, \( G_t \), can be given by [71]:

\[
G_t = 1/R_t = \frac{C_c|V_g - V_{th}| \mu}{L} \tag{12}
\]

The capacitance per unit length \( C_c \) of the CNT is given by:

\[
\frac{1}{C_c} = \frac{1}{C_q} + \frac{1}{C_g} \tag{13}
\]

where \( C_q \) is the quantum capacitance and \( C_g \) is the gate capacitance. The gate capacitance can be estimated using the model of the capacitance of a wire (nanotube) at a distance \( h \) from the gate, which is the oxide thickness plus the radius of the CNT, \( r \) [72]:

\[
C_g = \frac{2\pi L \varepsilon_r \varepsilon_0}{\ln(2h/r)} \tag{14}
\]

Since water has large dielectric constant, the gate capacitance of the CNT will increase due to the presence of water. Therefore, an enhancement of gate-nanotube coupling is expected when the
device is in an aqueous environment, which increases penetration of electromagnetic fields into the nanotubes [73]. As a result, the conductance of the CNTFET increases.

4.7 Design and Fabrication of Polydimethylsiloxane (PDMS) Channel

With most metallic traces and electrodes protected by the SU-8 protection layer, the CNTFETs no longer degrade in an aqueous environment. Therefore, measurements can be conducted in glucose solutions. The first experiment was to see the response of the CNTFET where no GOx had been adsorbed on it, and the CNTFET should not show any response towards a glucose solution. I first measured the transfer characteristics of CNTFET in 100 mM glucose solution. A significant change in the hysteresis and a slight increase in saturation current were observed, but these changes were similar to the device behavior in PBS. The comparison of the transfer characteristics is shown in Figure 4.11.
However, a similar response was seen with a CNTFET in PBS, and is thought to be due to the gate coupling effect in an aqueous environment. Then I measured the source/drain current of the CNTFET at a fixed gate voltage instead of sweeping the gate voltage. Without GOx, we should not observe any change of source/drain current when glucose solution is added to the CNTFET. In the experiment, I first applied a small droplet (≈5 µL) of PBS on the CNTFET and fix the gate and source/drain voltage to be -10 V and 20 mV, respectively, thereby “theoretically” creating a constant source/drain current (which is not seen in experiment, as shown in Figure 4.12). Then I added a drop (≈5 µL) of glucose solution to the PBS over the CNTFET. A change of current was observed when the drop of glucose solution comes into contact with the carbon nanotube, as shown in Figure 4.12.
Figure 4.12. Source/drain current increased upon adding glucose solution droplet, and it was not constant before and after the addition of the glucose solution.

It is also noticed that the source/drain current decreases before and after the delivery of glucose droplet. This experiment is repeated by continuing to add droplets of glucose solution to the solution over the CNTFET. A change of current is observed each time I deliver a droplet of glucose solution, as shown in Figure 4.13.

Figure 4.13. CNTFET response to the delivery of glucose droplets.
These experiments were repeated using PBS alone instead of glucose solution, and the results show a similar current versus time curve. It is therefore clear to see that the cause in the change of source/drain current is related not to glucose concentration, but rather to the change in the liquid volume. As discussed earlier, water has larger dielectric constant than air, thus the aqueous environment can increase the gate-CNT coupling [73]. This coupling is suddenly enhanced due to the delivery of the liquid, increasing the penetration of the electromagnetic field into the CNT. Thus the current increases suddenly. As the volume of the liquid droplet gradually decreases due to evaporation, the gate-CNT coupling is weakened gradually. Therefore the current slowly decreases.

In order to stabilize the gate-CNT coupling of the CNTFETs in an aqueous environment, the amount of the sample liquid should remain constant during the test. With the current set up, liquid droplets are directly applied onto the CNTFET with little to no volume control. Therefore adding droplets can greatly increase the volume of the liquid contacting the carbon nanotube. Moreover, since the droplet has a very small volume (∼5 µL), and is exposed to air, the evaporation of the liquid is very fast and it takes little time for the liquid to completely dry out.

To solve this problem, a simple closed liquid reservoir, or channel, is created using Polydimethylsiloxane (PDMS: Sylgard 184, 10:1 ratio) to encapsulate the CNTFET. With this configuration, the volume of the liquid over the CNTFET remains constant over the testing period. A diagram illustrating the idea is shown in Figure 4.14.
The width of the channel is 1 mm to encapsulate all the devices on the chip. The channel will be covering five different CNTFET devices at once. There are two reservoirs at the two ends of the channel, serving as liquid inlet and outlet. Syringes with luer lock fittings were used to deliver the solution. A schematic diagram is shown in Figure 4.15.

Figure 4.14. Concentration of the solution changes due to evaporation while the PDMS channel could prevent this; red dots represent glucose molecules.
The PDMS channel is fabricated by mixing the base and curing agent in a 10:1 ratio by weight, stirring until the mixture turns milky. However, this renders hydrophobic PDMS, and in order for the liquid to flow through the channel, the hydrophobic PDMS must be made hydrophilic. A usual way to achieve this is to plasma treat the PDMS surface in O$_2$. The drawback is that the hydrophilicity is very temporary. To generate a more lasting hydrophilic PDMS, I use Silwet L-77 purchased from Lehle Seeds to modify the wettability of the PDMS. Silwet L-77 is a surfactant designed to improve the wetting properties and it is often used on
crops so that they can absorb more water. It can convert PDMS from hydrophobic to hydrophilic [74]. The Silwet is an additive to the uncured PDMS, and comprised only 0.8% of the total weight of the base and curing agent. The mixture of pre-cured PDMS and Silwet is then poured into a mold for curing. The mold is made of stainless steel, a picture of which is shown in Figure 4.16 (a), and is used to create the PDMS channel reservoir, as shown in Figure 4.16 (b).

![Figure 4.16. A picture of (a) the mold of the PDMS channel and (b) the PDMS channel](image)

The mold consists of several removable parts so that the cured PDMS can be easily extracted from the mold. A picture of the cured PDMS channel is shown in Figure 4.16 (b). There are two large square reservoirs at the ends of the channel so that the solutions can be easily introduced into the channel. Figure 4.17 illustrated the PDMS channel being used for a device undergoing testing, where the source, drain, and gate electrodes are accessible to the probes for electrical measurements. To attach the PDMS to SiO₂ substrate, oxygen plasma treatment is often used. Oxygen plasma can improve the bonding between PDMS and SiO₂ by introducing roughened bonding surfaces and reactive chemical groups [75]. However, this bonding is
permanent, which is not suitable for our design. In this work, the PDMS is mechanically affixed to the silicon-based CNTFET in a reversible manner, without any plasma treatment. This allows the PDMS channel to be re-used for multiple sets of CNTFETs.

![Figure 4.17. A picture showing the devices under test using the PDMS channel, all on the probe station. The electrodes are accessible to the probes.](image)

One problem still persists with this set up namely there was leakage between the PDMS and the SiO$_2$ substrate. One reason for this is that when the PDMS channel is mechanically separated from the mold, the PDMS becomes somewhat deformed. Therefore, it cannot form a good seal with the SiO$_2$ therefore leading to liquid leakage. In order to solve this problem, a plastic cover is used to continuously push down on the flexible PDMS by using two screws, creating a good seal. The material used is plastic to prevent electric current leakage. Two syringe
needles with lure-locks are attached to the plastic cover, serving as the liquid inlet and outlet. A picture of the complete set up is shown in Figure 4.18.

Figure 4.18. A picture of the complete set up for the devices to be measured in liquid; the plastic beam is continuously pushed down on the flexible PDMS by using two screws bolted on a metal stage, the glass slide under the devices is used to insulate the gate from the metal stage

Using this set up, the effect of the evaporation on the conductance of the devices is eliminated. The source/drain current of the CNTFET at a fixed gate voltage is measured using this set up. The result shows that the conductance is fairly stable when the device is immersed in liquid. Figure 4.19 shows the $I_{SD}$ versus time curve of a device in PBS. The gate and source/drain voltage are set at -10 V and 20 mV, respectively.
Figure 4.19. Source/Drain current is stable in PBS when the PDMS channel is used; Inset shows the noise of the current

With the CNTFET electrodes successfully passivated using SU-8 and the encapsulation of fluids in the sensing region accomplished using PDMS, GOx incubation is needed before the glucose sensing experiments can be carried out. Details about the GOx incubation process is given in the next section.

4.8 Glucose Oxidase Incubation

Glucose Oxidase from Aspergillus niger is purchased from Sigma-Aldrich Co. LLC. Solutions of GOx are prepared by adding 100 mg GOx to 10 mL of PBS. GOx, being a protein, can nonspecifically attach to not only the sidewalls of the carbon nanotubes, but also to everywhere else it comes into contact. The whole substrate with different CNTFET devices was completely immersed in GOx solution stored in a beaker at 4 °C overnight for the enzyme to be
physically adsorbed onto the carbon nanotubes. Then the samples were rinsed and dried. An Atomic Force Microscopy image of GOx adsorbed onto the carbon nanotube is shown in Figure 4.20.

![Atomic Force Microscopy image of GOx adsorbed onto the carbon nanotube](image)

Figure 4.20. GOx is adsorbed onto the carbon nanotube and the substrate.

The height of the GOx molecules are measured using AFM, as is shown in Figure 4.21, and the size is measured to be around 8 nm. This result coincides with other reports of the approximated size of GOx, which is a compact spheroid (6 nm × 5.2 nm × 7.7 nm) [76].
Figure 4.21. (a) Height measurement is performed along the white line (A-A’)
(b) Measured size of GOx molecule to be around 8 nm

In this research, linking molecules are not used to attach the GOx molecules to the CNT since aqueous incubation of CNTs with a GOx solution, in the absence of linking molecules, can lead to a robust adsorption of GOx [77, 78].

After the non-specific deposition of GOx, a change in the transfer characteristics for all CNTFETs is evident and is predominantly due to the GOx that is adsorbed on the nanotube. For some ambi-polar devices, it was observed that a ‘bump’ occurred for positive gate voltages near 0 volts, as shown in Figure 4.22, and the reason behind this phenomenon remains unclear. One suggestion was that the deposition of GOx may create an extra state for electron transfer [Private communication with Dr. Smitha Vasudevan from George Washington University]. In order to verify this, I measured the transfer characteristic for the same device in vacuum to remove any gas and water molecules adsorbed on the CNT so that the hysteresis effect is eliminated. In addition, the device was measured under low temperature to remove the thermally assisted tunneling. Using this method, the channels of conduction can be clearly seen. If this bump is
indeed an extra state for electron transfer, it should be clearly observed after removing the hysteresis effect.

The measurement is conducted in a liquid nitrogen cryostat at a temperature of 77 K. The sample is first wire bonded, then it is mounted on an oxygen-free copper plate located on the sample stage of a low temperature probe. The sample stage is sealed in a brass vacuum container with an indium O-ring. This brass vacuum container is immersed in the liquid nitrogen and the sample is cooled down through a cold finger. A photo of the sample stage with a mounted chip is shown in Figure 4.23.
The low temperature measurement revealed that the ‘bump’ decreased over a period of weeks and finally disappeared under vacuum, as shown in Figure 4.24 (a), (b) and (c). The transfer characteristics under low temperature (77K) shows the quantum conductance plateaus. The quantum conductance plateaus show the conductance of semiconducting CNT depends on the number of conduction channels (a quantized conductance), as discussed in Chapter 2. However, the extra state caused by GOx adsorption is not observed, as shown in Figure 4.24 (d). This result differs from our assumption, which indicates that the bump is not an extra state for electron transfer created by the deposition of GOx. The cause of this phenomenon remains
unclear, as does the fact that this ‘bump’ occurs only for ambipolar devices after the GOx deposition.

Figure 4.24. (a) A ‘bump’ is observed after GOx incubation; (b) The ‘bump’ decreases after 3 weeks; (c) The ‘bump’ disappears under vacuum; (d) Transfer characteristic under low temperature.

4.9 Glucose Measurements Using CNTFETs

After the incubation process to non-specifically deposit GOx, the glucose detection experiments are conducted to test the effect of the GOx enzyme on the devices’ ability to sense
glucose. First, the transfer characteristics for the device in a 50 mM glucose solution is measured before it is incubated with GOx. The glucose solution is prepared by dissolving 90 mg glucose in 10 mL PBS. As expected, no difference in saturation current is noticed, as shown in Figure 4.25.

![Figure 4.25. Transfer characteristics of a device before the incubation of GOx in PBS (black curve) and in 50 mM glucose solution (red curve)](image)

The same device is then incubated in GOx solution using the procedure described in section 4.6 (This GOx incubation process is the same for all experiments). A schematic of where the GOx molecules end up after the incubation is shown in Figure 4.26. The same experiment is conducted after the GOx incubation and the saturation current increases when the device is exposed to a 50 mM glucose solution, as shown in Figure 4.27. This result shows that the presence of GOx on the CNTFET enables the device to sense glucose.
The response of GOx incubated CNTFET devices towards glucose is measured for different glucose concentrations, where the devices have been protected with an SU-8
passivation layer and a PDMS channel. Measurements with CNTFET devices without Au nanoparticles are first conducted.

The devices are exposed to glucose solutions having different concentrations by introducing them into the PDMS channel where the glucose molecules can react with the GOx attached to the CNT sidewall. The transfer characteristics are measured for each glucose concentration and it is found that the saturation current increases with the increase of glucose concentration. As shown in Figure 4.28, the transfer characteristics of the device is first measured in PBS. The device is rinsed with DI water and dried with nitrogen before the next curve is measured in a 12.5 mM glucose solution. An increase of the saturation current is noticed. Then the same procedure is repeated with glucose solutions of 25 mM, 50 mM, and 100 mM. The saturation current increases each time with a higher glucose concentration. As discussed earlier, the glucose-GOx reaction produces electrons, which should dope the p-type CNT and thus shift the threshold voltage toward the negative gate voltage side. However, due to the increased hysteresis, this effect could not be observed.
It should be noted that after each rinse and dry step, the transfer characteristics are measured again to see if the device can recover back to its previous condition. As shown in Figure 4.29, the transfer characteristics remains relatively close to the base line, with the difference in saturation currents being within 6 nA.
Another CNTFET device was decorated with Au nanoparticles, then passivated with SU-8 and incubated with GOx. The transfer characteristics are measured with each glucose concentration using the same procedure as the device without Au nanoparticles. The results are shown in Figure 4.30. Unlike the device without Au nanoparticles, the saturation current decreases with the increase of glucose concentration. As before, the transfer characteristics of the device between each measurement are shown in Fig. 4.31 that is after the rinse and dry step. Also unlike the device without Au nanoparticles, where most curves tend to follow the baseline, here the saturation current appears to decrease away from the baseline after each measurement.
Figure 4.30. Transfer characteristics of the device in PBS (black curve), 12.5 mM glucose solution (red curve), 25 mM glucose solution (blue curve), 50 mM glucose solution (green curve).

Figure 4.31. Transfer characteristics of the device before the measurements, which serves as the base line (black curve), transfer characteristics of the device that is rinsed and dried after the exposure to PBS (red curve), 12.5 mM glucose solution (blue curve), 25 mM glucose solution (green curve), 50 mM glucose solution (purple curve).
Since after each measurement and before the next measurement, the device is rinsed with DI water and dried, a new base line is therefore acquired. Note that the rinsing step could also remove GOx, though not completely. In order to see the actual response, the transfer characteristics in different glucose concentrations need to be compared with each new base line. Therefore the actual response curves for the device without Au nanoparticles are shown in Fig. 4.32 where the baseline curves are the same as those in Figure 4.29. These are compared with the response curves for the device with Au nanoparticles, as shown in Fig. 4.33. Although the device with Au nanoparticles showed a decrease in saturation current (Fig. 4.30), the relative change in the saturation current actually increases compared to the new base lines, as shown in Fig. 4.33. Therefore both devices show an increase in saturation current with the increase in glucose concentration. In order to better visualize the change in the saturation current more clearly, the relative difference in saturation current is plotted versus different glucose concentrations for both devices, as shown in Fig. 4.34. As we can see, the device without Au nanoparticles shows a trend in the difference in saturation current. When the glucose concentration increases, the difference in saturation current also increases. However for the device with Au nanoparticles, there is no obvious trend.
Figure 4.32. The transfer characteristics of the device without Au nanoparticles before each measurement (black curves) and in different glucose concentrations from 0-100 mM (red curves).
Figure 4.33. The transfer characteristics of the device with Au nanoparticles before each measurement (black curves) and in different glucose concentrations from 0-50 mM (red curves)
In conclusion, the CNTFET devices have shown a response towards the increase of glucose concentration. For the device without Au nanoparticles, we see a constant increase in the saturation current with the increase of glucose concentration. For the device with Au nanoparticles, we see a larger response towards glucose, however in the opposite direction. This effect is more clearly seen when new base lines are acquired. The actual glucose sensing mechanism of the devices, as well as the reason why we are seeing an opposite response using Au nanoparticles, are still unclear. Therefore further investigation is needed. One possible reason for the drop in source/drain current of the device with Au nanoparticles is that since biomolecules can easily attach to Au nanoparticles and form a strong binding, the byproducts of the reaction may also attach to the Au nanoparticles and are very hard to rinse off. These
molecules act as the carrier scattering sites and thus decrease the saturation current after each measurement, as shown in Fig. 4.31. When the concentration is higher, there are more adsorption events take place and thus we see a constant decrease in the saturation current after each measurement, with the increase of the glucose concentration.

In order to better investigate the glucose sensing abilities of the CNTFETs, a liquid gate could be used instead of a back gate. Since the sensing of glucose occur in aqueous environment, the liquid can be used as a very efficient gate for the immersed CNTs [79]. The liquid gate is much more effective compared with back gate due to a much larger gate capacitance [71]. It also provides a much better control of the gate voltage applied to the CNTs since the liquid gate voltage does not depend on the liquid composition. The use of liquid gate will be included in the future work, either to provide a fixed gate potential or to incorporate a reference electrode.
CHAPTER 5
AU NANOPARTICLES ON CNTFETS FOR GAS SENSING

In addition to glucose sensing, Au nanoparticles can also be used to investigate the gas sensing mechanism of CNTFETs. Au nanoparticles are deposited onto semiconducting carbon nanotubes to form local Schottky barriers. An SU-8 passivation layer is employed to eliminate the effect of the adsorption of gas molecules on metal electrodes. Gas measurements using CNTFETs with and without Au nanoparticles are conducted and the results are compared with our previous work.

5.1 Introduction of CNTFETs Gas Sensing

CNTFETs have been used for gas sensing applications and have shown great promise as a possible alternative for conventional gas sensing products currently on the market, such as gas sensors based on chemicals that would change color upon reacting with target gases, and gas sensors based on resistive thin films that would change resistance upon adsorption of the gas molecules [80]. CNT based gas sensors are very attractive due to their high sensitivity to gases, the ability to operate at low current thresholds and the ability to function in standard conditions for temperature, pressure, and humidity [81]. Due to all these advantages, the gas sensing properties of CNTs have been widely studied over the past years. However, there is still controversy on the actual gas sensing mechanism of the CNTFET. There are two main possible mechanisms. One is through charge transfer due to the adsorption of gas molecules onto the CNT
side wall [82]. The other is the modulation of the Schottky barrier between the CNT and metal electrode contacts [83].

The work function of a metal is the minimum energy needed to remove an electron from the surface of a metal to a point in the surrounding vacuum ambient. Gases can induce changes in the work function of metals by withdrawing or donating electrons and change the surface charge on the metal [84]. This change in charge will create electric dipoles at the surface, which affects the amount of energy needed to remove an electron from the metal and thus change its work function. This will in turn modify the Schottky barrier at the CNT-metal junction and therefore change the conductance of the CNTFET [84].

Previous work in our group has demonstrated that Schottky barrier modulation is the main detection mechanism in CNTFET gas sensing [83]. The single tube CNTFET gas sensor study we conducted tested two gases: nitrogen dioxide (NO₂), which is an electron acceptor, and ammonia (NH₃), which is an electron donor. When the CNTFET is exposed to NO₂, the conductance of the p-type device increases and when the same CNTFET is exposed to NH₃, the conductance of the device decreases.

The single CNT device was tested by covering the metal contacts with photoresist, leaving only the CNT surface exposed. When such devices were exposed to NO₂, they didn’t immediately exhibit any changes in their transfer curves due to the protection of metal electrodes by photoresist, but rather respond only after the NO₂ has had time to diffuse through the photoresist layer. In contrast, devices without photoresist protection over their contacts respond immediately after gas exposure [83].
However, when testing devices made with CNT networks, it was found that even with the metal electrodes covered with photoresist, the devices still respond to gas exposure. As-grown CNT networks using chemical deposition method are usually a mix of both metallic and semiconducting tubes [84]. The presence of the metallic CNTs shorting the two electrodes causes a large background current that is independent to an applied gate voltage, leading to a less ideal transfer characteristic. Therefore, before the gas measurements were performed, a selective electrical breakdown was necessary in order to remove the metallic CNTs from the network [69]. This selective electrical breakdown procedure breaks down the metallic CNTs using a large amount of current through the metallic CNTs, while the semiconducting CNTs stay intact because they are set to the OFF-state. More specifically, the gate voltage is set at a value for the semiconducting CNTs to stay in the OFF-state. Then a large source/drain voltage is applied to the source/drain electrodes. Since the semiconducting CNTs are in the OFF-state, there is no current flowing through them while there is a large amount of current flowing through the metallic CNTs. This current will create joule heating that could raise the temperature of the CNT to 600 °C. Under this high temperature, the C-C bond is broken due to desorption of CO in the presence of oxygen, leading to the degradation of the metallic CNT [43]. Thus, only the semiconducting CNTs are connected between the source and drain electrodes of the CNTFET, with the open-circuited metallic CNTs contacting the semiconducting CNTs. Then the whole device, including the covered metal electrodes and CNT junctions are exposed to NO₂. The devices show immediate response towards NO₂, similar to un-passivated single CNT devices tested [84].
This indicates that the presence of the CNT-CNT junctions plays a major role in the device response. There are two types of junctions contributing to the change in conductance. First, when two semiconducting CNTs are in contact, tunnel barriers form at the junctions between the semiconducting CNTs. In addition to this tunnel barrier, Schottky barriers also form at the junctions of metallic CNTs and semiconducting CNTs [85]. The gas molecules adsorbed at the CNT-CNT junctions will change the local doping at the junctions and thus change the local Schottky barriers, leading to the change in conductance immediately after gas exposure [86, 87]. Of course, the CNT-metal electrode junctions will continue to be involved in gas sensor responses.

In addition, the number of CNT-CNT junctions plays an important role in the change of conductance when exposed to gas. When the number of the nanotube junctions is high, the junctions dominate the response. When the number of the nanotube junctions decreases, their role in the overall response diminishes and the electrodes start to play a more major role in the response, similar to single nanotube devices.

This data can be corroborated by employing Au nanoparticles deposited onto a single semiconducting carbon nanotube to form local Schottky barriers. In this way, the experiments with metal-semiconducting CNT junctions can be mimicked by Au nanoparticle-semiconducting CNT junctions to show the same effect as that seen in network devices with Au decorated single CNT devices.
5.2 Gas Measurements Using CNTFETs with and without Au Nanoparticles

The first step is to completely remove the effect of the metal electrodes by passivating them with photoresist so that the gas molecules do not interact with the electrodes immediately. Here, I used SU-8 photoresist to protect the electrodes from gas molecule adsorption, the details of which have been given in Chapter 4. After the Au electrodes are completely covered by SU-8, testing of the gas sensing can be conducted first for an undecorated CNTFET, followed by a Au decorated CNTFET. The experimental set up consists of a plastic tank with a gas inlet and outlet. The inlet is connected to a compressed gas cylinder through a rotameter and the outlet is connected to a vacuum pump so that the gas concentration in the tank is held constant during the test. The sample is placed on the stage of the probe station, which resides inside the plastic tank. A schematic of the set up is shown in Figure 5.1.

![Figure 5.1. Schematic of the gas measurement set up](image)

The device is connected to three probes corresponding to the source, drain and gate electrode respectively. The source-drain voltage ($V_{SD}$) applied is 20 mV. The gate voltage ($V_G$)
is swept between -10 V and 10 V, in increments of 0.1 V. The source-drain current ($I_{SD}$) is first measured as a function of $V_G$ for 10 minutes in air to ensure that the conductance of the device is stable. Then the device is exposed to NO$_2$ through the inlet hose connected to a NO$_2$ cylinder and the transfer characteristics of the device is recorded. In addition, the saturation conductance is also recorded as a function of time to show the response towards gas more clearly. The saturation conductance is selected to be the conductance at $V_G = -9.8$ V since it is close to the highest conductance without being affected by the noise produced by the hysteresis loop changing directions [88]. For the undecorated CNTFET, the device is exposed to NO$_2$ for 6 minutes and the result indicates that an increase of the saturation current is minimal, as shown in Figure 5.2 (a).

The same device is then decorated with Au nanoparticles and the same gas measurement is repeated. There are approximately 20 Au nanoparticles on the CNT. This time, the results show that the change in saturation current is significant, as shown in Figure 5.2 (b). The comparison of the two saturation conductance is shown in Figure 5.3. It is clearly seen that the deposition of Au nanoparticles significantly increases the device response towards NO$_2$, which matches our assumption that the change in local Schottky barriers is the main mechanism for gas sensing of CNT network devices.
Figure 5.2. Transfer characteristics of the device in air and in NO₂ where (a) CNT without Au nanoparticles; (b) CNT with Au nanoparticles.

Figure 5.3. Change in saturation conductance versus time. Black curve represents the device without Au nanoparticles and red curve represents the device with Au nanoparticles.
The same measurements were conducted using NH$_3$ instead of NO$_2$, and similar results are obtained, namely the device shows a greater response towards NH$_3$ when the CNT has been decorated with Au nanoparticles. The difference is when exposing to NH$_3$, the conductance of the device decreases, as shown in Figure 5.4. The comparison of the saturation conductance is shown in Figure 5.5.

Figure 5.4. Transfer characteristics of the device in air and in NH$_3$ (a) device without Au nanoparticles; (b) device with Au nanoparticles
Previous work in our group shows that when the number of the nanotube junctions increases, the device shows a greater response towards gas exposure. Since these nanotube junctions can be replaced by Au nanoparticle-CNT junctions, as shown earlier in this chapter, it will be interesting to gradually increase the number of the Au nanoparticles on the CNT side wall using the site-specific deposition method described in Chapter 3 and compare the results with our previous work. This experiment will be conducted in the future.
CHAPTER 6
CONCLUSION AND FUTURE WORK

In this research, a back gate CNTFET geometry is used for glucose and gas molecule sensing due to its ease of fabrication and the sensible detection mechanism. CNTFETs are fabricated on Si/SiO$_2$ substrates using advanced nano-fabrication techniques including e-beam lithography and sputtering. Electrical characterization is performed using a four-probe micromanipulator system.

A simple in-situ electrochemical method to target the deposition of gold, as well as other metallic nanoparticles along a CNTFET is introduced in this research. The size of the Au nanoparticle can be controlled from 10 nm to over 100 nm. This method provides better control and is much easier to carry out compared to other site-specific deposition techniques. When a Au nanoparticle is deposited onto a semiconducting CNT, a local Schottky barrier is created on the CNT side wall, acting as an electron scattering site.

Au nanoparticles are used to study the glucose detection capability of CNTFETs incubated with GOx, due to their ability to reorient the GOx molecules to a preferable direction when they are adsorbed onto Au nanoparticles, shortening the distance the electrons need to travel. An SU-8 passivation layer and a PDMS fluidic channel are also used to enable the proper function of the CNTFETs in an aqueous environment. Experimental results show that the presence of GOx on CNTFET enables the CNTFETs to respond towards glucose. However for the devices decorated with Au nanoparticles, a larger response in the other direction is observed.
The reasons why the saturation current of the devices increased towards the increase of glucose concentration, as well as the reason why we are seeing an opposite response using Au nanoparticles, are still unclear. Therefore further investigation is needed.

In addition to glucose detection, Au nanoparticle deposition are also used to study the gas sensing mechanism of the CNTFET. It is observed that the deposition of Au nanoparticles significantly increases the device response towards NO$_2$ and NH$_3$, which matches our assumption that the change in local Schottky barriers is the main mechanism for gas sensing of CNT devices.

There remain several open questions to answer. First, the actual glucose sensing mechanism of the CNTFET devices needs to be further investigated. Whether the response is due to direct electron transfer from the glucose oxidase molecules to the CNT or whether it is due to the modification in the potential barriers in Au nanoparticle-CNT junctions is still unclear.

Second, a possible obstacle for the glucose measurement is that the increase in glucose concentration may increase the dielectric constant of the solution, which leads to an enhancement of the gate-nanotube coupling. Since the electron transport in a CNTFET is very sensitive towards the environment, this change in the gate-nanotube coupling strength may affect the transfer characteristics. Therefore, the interaction between the glucose and GOx cannot be observed due to the dominating change in the gate-nanotube coupling. Moreover, since the hysteresis effect becomes significant when testing the devices in an aqueous environment, the effect of the electron doping (shift in threshold voltage) cannot be observed.

In future work, the following experiments would be conducted to answer the questions described above. First, in order to better investigate the glucose sensing mechanism of the
CNTFETs, a liquid gate could be used instead of a back gate. Since the sensing of glucose occurs in aqueous environments, the liquid can be used as a very efficient gate for the immersed CNTs. The liquid gate is much more effective compared with back gate due to a much larger gate capacitance [71]. It also provides a much better control of the gate voltage applied to the CNTs since the liquid gate voltage does not depend on the liquid composition.

Second, a microfluidic pump incorporating the PDMS channel could be used to deliver glucose solution into the channel. In current set up, the liquid can only be delivered manually using a syringe, which increases the difficulty of the experiment. In addition, due to the volume constrain of the reservoir, it is impossible to keep adding solutions to the channel, thereby changing the glucose concentration while testing. By using a microfluidic pump, the concentration of the solution can be easily controlled.

Third, a CNT network can be used as the semiconducting channel instead of a single CNT. Since every CNT is different in its physical (length, number of defects) and electrical (saturation current, threshold voltage) properties, it is very hard to achieve uniformity if a single CNT is used. For example, the voltage applied to the sacrificial electrode that can reduce Au ions onto one CNT may not be able to reduce Au ions onto another CNT. Another example is that due to the difference in saturation current and OFF-state current, it is not possible to use the data obtained from these devices as comparison. These problems causes difficulties in the fabrication, as well as the characterization processes. By going macroscopic, that is, to use a CNT network, it is possible to achieve uniformity in the properties of the devices. Moreover, the large surface area of the CNT network allows more GOx to be adsorbed, thereby further enhance the sensitivity of the CNTFETs.
Lastly, for the gas sensing applications, site-specific Au nanoparticle deposition can be used to further study the gas sensing mechanism of the CNTs. Previous work in our group shows that when the number of the nanotube junctions increases, the device shows a greater response towards gas exposure. Since these nanotube junctions can be replaced by Au nanoparticle-CNT junctions, as shown in Chapter 5, it will be interesting to gradually increase the number of the Au nanoparticles on the CNT side wall using the site-specific deposition method described in Chapter 3 and compare the results with our previous work.
APPENDIX A
INFLUENCE OF ARGON ON CVD-GROWN IN-PLANE SINGLE-WALLED CARBON NANOTUBE MESHES
(Published in IEEE, Microsystems for Measurement and Instrumentation, 2013)

The influence of argon on the growth of in-plane single-walled carbon nanotube meshes using chemical vapor deposition was investigated in collaboration with Dr. Marcio Fontana from Department of Electrical Engineering, Federal University of Bahia, Brazil [10]. We verified that the introduction of argon influences the diameter distribution and the field emission properties of the single-walled carbon nanotubes.

Chemical vapor deposition is the most popular method of producing SWCNTs at the present time. As described in Chapter 2, the process involves the flow of hydrocarbon vapor through a heated quartz tube. In addition, the introduction of a new gas entity in the typical CVD process can induce changes on morphological and physical properties of the SWCNTs.

The addition of the argon flow has been shown to produce high quality double-walled carbon nanotubes (DWCNTs) in one-step by the catalytic CVD [89]. It was verified that argon plasma produces an efficient etching and cleaning process on the as-grown multiwall carbon nanotubes. The structural improvement in the MWCNTs was strongly confirmed by other groups as an increase in the emission current and a reduction in the turn-on voltage [90]. In the case of SWCNT, argon flow has been studied by many groups. However, to our knowledge, no study has focused on the influence of argon on field emission properties of SWCNT meshes deposited in hydrogen-rich and hydrogen-poor mixtures. In this work, we studied the effect of the addition of argon on the deposition of in-plane SWCNT mesh structures using a CVD furnace with a
mixture of methane, hydrogen and argon. We verified that the use of argon influences the
diameter distribution and the field emission properties of the SWCNTs. Morphological data,
obtained by field emission scanning electron microscopy, micro-Raman spectroscopy, and field
emission characterization are discussed.

Synthesis of carbon nanotubes was carried out as follows. The catalyst preparation was
adapted from the fabrication process of carbon nanotube field effect transistors. 1.6 mg ferric
nitrate nonahydrate (Fe(NO$_3$)$_3$•9H$_2$O) and 0.5 mg Molybdenum diacetylacetonate dioxide
(MoO$_2$(acac)$_2$) and 15 mg aluminum oxide were dissolved in 20 ml methanol to form the catalyst
solution. Catalyst was spin coated onto the SiO$_2$ substrate at a spin rate of 1500 rpm. Carbon
nanotubes were grown using controlled chemical vapor deposition processes. A
methane/hydrogen/argon gas mixture (total flow 60 sccm) was initiated for a duration of 30
minutes for all experiments. The methane flow was kept constant at 32 sccm in the experiments
but the argon: hydrogen concentrations varied from 0:100 vol% to 90:10 vol%. All Samples
were analyzed by FESEM and Raman spectroscopy. Figure A1 shows typical top-view FESEM
images of as-synthesized samples produced by the CVD process.
Figure A1. SEM images from samples using different argon concentrations:
(a) 0 vol\%, (b) 50 vol\%, (c) 90 vol\%.
Raman spectroscopy is a powerful characterization technique that can provide information about the properties of the materials such as the identification of molecules and crystal orientation [91]. Raman spectroscopy is based on Raman scattering, which is the inelastic scattering of light with the materials. The intensity of the scattered light is plotted in a Raman spectra as a function of the frequency shift, which corresponds the energy lose. This energy lose is closely related to the material properties, which can be studied through the Raman spectra.

Figure A2 shows Raman spectra of the samples deposited at different argon concentrations. We observed two typical SWCNT peaks located at 1350 cm\(^{-1}\) (D-band) and 1590 cm\(^{-1}\) (G-band). The G-band is an intrinsic feature of CNTs. It is closely related to the vibrations in sp\(^{2}\) carbon bond. The D-band is related to the scattering from defects, therefore provides information on the quantity of the defects. We also observed two weak peaks feature at 1581 cm\(^{-1}\) [curves (a), (b) and (c)] and 1568 cm\(^{-1}\) [curves (d) and (e)] that are characteristics respectively of the metallic and semiconducting SWCNTs [92]. The increase in D-band intensity suggests that by using argon in the CVD furnace, it increases the number of the defects on the CNTs.
Figure A3 shows typical intensity ratio of D-band to G-band (I_D/I_G). We observed I_D/I_G was proportionally related to the argon concentration in the gas mixture. SWCNT samples show intensity ratio of D-band to G-band ranging from 12% to 92% for different argon: hydrogen concentrations ranging from 0:100 vol% to 90:10 vol%. In addition, at higher argon concentrations (75 vol% and 90 vol%), the intensity ratio of D-band to G-band shows no significantly change (97% and 92%). This result corroborates with previous work [93], where the disorder in sp² hybridized carbon networks is similar to the in-plane oscillation of carbon atoms in the sp² graphite sheet of SWCNTs.
Figure A3. Typical intensity ratio of D-band to G-band

Figure A4 shows typical Radial Breathing Mode (RBM) peaks ranging from 100 to 300 cm$^{-1}$. The RBM mode is a phonon mode for which all the carbon atoms vibrate in the radial direction. Since the RBM frequency is inversely proportional to the CNT diameters, it is used to estimate the diameter of SWCNT [94]. Samples produced in hydrogen-rich mixtures (argon concentration < 25 vol%) had different RBM peaks [curves (a) and (b)] indicating higher diameter distribution while the samples produced in hydrogen-poor mixtures (argon concentration > 25 vol%) presented only a smooth peak [curves (c), (d) and (e)] indicating regular diameter distribution of SWCNTs. Table A1 shows details of the diameter distribution of SWCNTs synthesized at different argon concentrations in the furnace. The diameter distribution of the carbon nanotubes ranges between 1.0 nm and 2.2 nm depending on the different argon concentrations. Using argon provides smaller diameters as compared with those when pure
hydrogen is used. Varying the argon: hydrogen concentrations from 0:100 vol% to 90:10 vol% changes the diameter distribution to lower values. This result corroborates well with the data from previous work [95], where carbon nanotube diameter distribution was also found to decrease in the presence of argon gas.

Figure A4. Typical RBM peaks of the samples after deposition using different argon concentrations in the furnace. (a) 0 vol%, (b) 25 vol%, (c) 50 vol%, (d) 75 vol% and (e) 90 vol%.
<table>
<thead>
<tr>
<th>Argon:Hydrogen concentrations (Vol%)</th>
<th>RBM bands (cm⁻¹)</th>
<th>Diameters (nm)</th>
<th>Relative intensity of the RBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:100</td>
<td>124 133 148 167 189 198 208 259</td>
<td>2.2 2.1 1.8 1.6 1.4 1.3 1.2 1.0</td>
<td>w m w m m w w s</td>
</tr>
<tr>
<td>25:75</td>
<td>137 162 188 198 231 245</td>
<td>2.0 1.7 1.4 1.3 1.1 1.0</td>
<td>w m s w w</td>
</tr>
<tr>
<td>50:50</td>
<td>179 229</td>
<td>1.5 1.1</td>
<td>w w</td>
</tr>
<tr>
<td>75:25</td>
<td>229</td>
<td>1.1</td>
<td>w</td>
</tr>
<tr>
<td>90:10</td>
<td>229</td>
<td>1.1</td>
<td>w</td>
</tr>
</tbody>
</table>

Table A1. The diameter distribution of SWCNTs synthesized at argon concentration. (w: weak, m: medium and s: strong)

Figure A5 shows typical current–voltage characteristic curves of as-synthesized samples using different concentrations of argon. We observed that an increase in argon concentration in the gas mixture resulted in a corresponding decrease in the threshold voltage necessary to initiate field emission. We suggest that this behavior is a typical dependence of the electric field enhancement factor that increases according to the cathode radius of curvature at the point of emission where the SWCNT diameter decreases. The onset electrical field for a detected emission current of 1.0 µA for 0 vol%, 50 vol%, and 90 vol% argon concentration occurs at 6.5, 4.5, and 4.4 V/µm, respectively. We also observed oscillations in measured electron currents like “turn on – turn off” for higher argon concentrations. Similar to [96], we suggest that the emission
results from the body of the SWCNTs. This phenomenon may also be due to defects on the outer wall.

Figure A5. Measured electron currents versus voltage: (a) 0 vol%, (b) 50 vol%, and (c) 90 vol%

Figure A6 shows the typical Fowler–Nordheim diagram for samples using different argon concentrations, measured for a fixed cathode–anode distance of 75 μm. The linearity in the \( \ln(I/V^2) \sim (1/V) \) for SWCNTs samples indicates that the measured current is indeed the result of field emission [97].
In conclusion, the influence of argon on the growth of in-plane SWCNT meshes using CVD is investigated. Raman spectroscopy measurements performed in this work demonstrate clearly that SWCNT produced with different argon concentrations in the furnace have different diameter distributions. We demonstrated that it was possible to obtain SWCNTs with good field emission characteristics using CVD with a methane/hydrogen/argon mixture. The threshold voltage to electron emission was significantly decreased by higher argon concentration due to higher layer conductivity of the samples. In contrast, excess argon during the growth process showed to have negative effect on the SWCNT morphology with respect to field emission properties. Finally, our results encourage us to further explore the effect of argon on growth of SWCNT meshes, which lie parallel to the substrate surface, for field emission applications.
APPENDIX B
HYSTERESIS MODELING IN BALLISTIC CARBON NANOTUBE FIELD EFFECT TRANSISTORS
(Published in Nanotechnology, Science and Applications, 2014)

Hysteresis is a peculiar effect in CNTFETs and is difficult to predictably analyze due to the different nonlinear effects that are present. Mathematical models have been developed to characterize hysteresis behavior, such as the limiting-loop proximity ($L^2P$) [98], Preisach [99] and Jiles-Atherton [100] models. However, using only these models individually has not generated accurate approximations for CNTFET drain current versus gate voltage, or $I_{DS}-V_{G}$ electrical characteristics primarily because they do not take into account the specific properties of the nanotube. One theoretical model used to describe carbon nanotube field-effect transistors was proposed [101], based on the physical effects of ballistic conduction, where electrons in the nanotube are not affected by scattering [102]. Ballistic transport has nearly been achieved in CNTFETs by the use of proper contact materials such as Pd and Au, thereby reducing transport barriers and approaching the theoretical conductance limit of the device ($G_{on} \approx 4q^2/h$) [103].

In collaboration with Dr. Marcio Fontana’s group from the Department of Electrical Engineering, Federal University of Bahia, Salvador, Brazil, we developed a relatively reliable mathematical model to determine drain current by considering the physical basis of CNTFET conduction, which includes the hysteresis effect [104]. Experimental data was obtained from five devices, the first of which was used to demonstrate the hysteresis effect during a gate voltage sweep, the second was used to corroborate simulation data from the theoretical model with experimental results for different gate voltage ranges. The others were modeled in order to verify
the effectiveness of the model, and the simulation results are presented in a Table B2. Positive results were obtained, considering that some fitting parameters required estimation while instrument accuracy affected some of the values obtained.

Due to its dimensions, a carbon nanotube can be considered as quasi-1D element, whose diameter and chirality directly affect its properties. There is no boundary scattering in pristine nanotubes due to the lack of surface bonds and a cylindrical structure. Thus, for short length nanotubes, quasi-ballistic transport can be observed [105]. In his work, all the devices have a CNT channel length of 1 µm to 2 µm that allows quasi-ballistic transport.

For a CNTFET, when contact is made between the CNT and the metal electrodes, a Schottky barrier is formed at the metal-CNT junction. This barrier has a height related to the work function of the metal electrode. Since Au was used as the contact material in our experiments, which has a large work function, the Schottky barrier height becomes small. A schematic diagram is shown in Figure B1. Hence, we only consider the ballistic transport within the CNT channel and assume that the gate voltage only modulates the energy bands of the CNT channel between the source and drain [101].
The channel potential can be described as:

$$\phi_s = \begin{cases} V_G, & V_G < \Delta 1 \\ (V_G - \alpha(V_G - \Delta 1)), & V_G \geq \Delta 1 \end{cases}$$

(15)

where $\phi_s$ is the channel potential, $V_G$ is the gate bias, $\alpha$ is the slope of the drain current curve and $\Delta 1$ is the equilibrium minima for the first sub-band.

In order to remove the discontinuity at $\Delta 1$, the following equation is proposed [106]:

$$\phi_s = V_G - \frac{\alpha(V_G - \Delta 1) + \sqrt{(\alpha(V_G - \Delta 1))^2 + \varepsilon^2}}{2}$$

(16)

with $\varepsilon$ serving as a user defined smoothing parameter (typically around 0.5 V).

Figure B1. Two different metal electrodes contacting with a same CNT. The Schottky barrier formed at the junction of the CNT and the metal with lower work function, as shown in (a), is larger than that formed at the junction of the CNT and the metal with higher work function, as shown in (b). Note: $W_a$ and $W_b$: work function of metal a and b, $\Phi_{SBa}$ and $\Phi_{SBb}$: Schottky barrier formed at the junctions. $E_{FM}$ and $E_{FC}$: Fermi level of the metal and the CNT. $W_a < W_b \rightarrow \Phi_{SBa} > \Phi_{SBb}$
The slope of the characteristic curve, α, is expressed as a polynomial of $V_{SD}$ such that

$$\alpha = \alpha_0 + \alpha_1 V_{SD} + \alpha_2 V_{SD}^2,$$

where $\alpha_0$, $\alpha_1$, and $\alpha_2$ are dependent on both CNTFET diameter, $d$, and gate oxide thickness, $t_{ox}$ [107]. The drain current, $I_D$, can now be determined by the simplified expression below:

$$I_D = \frac{4qkT}{h}[\ln(1 + e^{\xi_S}) - \ln(1 + e^{\xi_D})] \quad (17)$$

where

$$\xi_S = \frac{\phi_S - V_{TH}}{V_t} \quad (18)$$

and

$$\xi_D = \frac{\phi_S - V_{TH} - V_{CN}}{V_t} \quad (19)$$

with $V_{TH}$ is the threshold voltage, and the thermal voltage defined by

$$V_t = \frac{kT}{q} \quad (20)$$

where $k$ is the Boltzmann constant, $q$ is the electron charge, and $T$ is the temperature.

Hysteretic effects cause a shift of the threshold voltage, which may be considered as the first sub-band, $\Delta 1$. Experimentally, a sweep to large positive values of $V_G$ creates a positive shift in the threshold voltage [108, 109, 110], and $V_{SD}$ does not affect the shift or the position of the curves. According to the variables set forth in the L²P model [98], hysteresis is characterized by a horizontal shift between the two curves, denoted as $w$, which designates the magnitude of shift around a central voltage, $V_C$, along the horizontal axis, as shown in Figure B3. An auxiliary variable, $\delta$, can be used to identify hysteresis orientation, which is the same as the $V_G$ sweeping orientation. These variables are all experimentally obtained. In the case of CNTFET, without
these parameters shown above, the current model cannot show hysteresis. Adapting the threshold voltage to the $L^2P$ model variables, these effects become evident.

Applying these definitions:

\[ V_{TH}(w, V_C) = \delta \frac{w}{2} - V_C \]  

(21)

with

\[ \delta = \begin{cases} +1, & \text{for } \frac{dV_G}{dt} > 0 \\ -1, & \text{for } \frac{dV_G}{dt} < 0 \end{cases} \]

(22)

Although carbon nanotubes are described as having ballistic behavior, the contact resistance between the electrode and the carbon nanotube [111] affects the ON-state current level because the drain-source voltage in the nanotube is just a fraction of $V_{SD}$ applied to the transistor. By voltage division of 3 series-connected resistances.

\[ V_{CN} = \frac{R_{CN}V_{SD}}{R_{CN} + R_D + R_S} \]

(23)

where $R_{CN}$ is the intrinsic resistance for the carbon nanotube, which is ideally determined as $h/4q^2$ (approximately 6.4kΩ) [101], while $R_D$ and $R_S$ are the drain and source contact resistances, respectively.

Figure B2 illustrates the conceptual procedure for CNTFET modeling, where $w$ and $V_C$ are obtained from the $L^2P$ model while the other variables arise from ballistic model.
Experimental data in this research was obtained from CNTFETs using the fabrication process described earlier in this chapter. In addition, Micro-Raman spectroscopy was carried out to measure the Raman spectrum of the CNTs at room temperature using a Renishaw Raman microscope (inVia; Renishaw, Wotton-under-Edge, UK) employing the output of an Ar+ laser (20 mW power) for excitation at $\lambda=514.5$ nm. All devices were measured at room temperature (300 K) in a controlled pressure (1 atm + 0.12 kPa in H$_2$O) and humidity (30%) environment.

For the determination of the L$^2$P model parameters $w$ and $V_C$, we used graphic analysis based on the transfer characteristics of the CNTFETs obtained experimentally. Figure B3 describes the link between these parameters and their visual representation in the device transfer characteristics. $w$ is the horizontal distance between the two segments of the curve, obtained by tracing two tangential along the slope of the two portions of the curve in the transition region.
Thereafter, $V_C$ is obtained by determining the horizontal midpoint of $w$ at the vertical point located in the OFF-state saturation current value.

Although $\alpha_0$, $\alpha_1$, and $\alpha_2$ are inherent to the physical characteristics of the CNTFET, as mentioned above, there is no known mathematical relation that could allow the prior acquisition of these parameters. Thus, we considered each transistor as an independent device, obtaining the slope of the curve in the transition region for each device and drain-source voltage by the minimization of deviations between the data and the model curves in this region. In this way, with at least three measurements of $\alpha$ for different values of $V_{SD}$, it is possible to determine $\alpha_0$, $\alpha_1$, and $\alpha_2$ for a device by a linear system.

Figure B3. $I_{SD}-V_G$ curves with hysteresis and obtainment of parameters $w$ and $V_C$.

Figure B4 (A) and (B), respectively, show typical Raman spectrum and radial breathing mode peaks, respectively, ranging from 100 to 300 cm$^{-1}$ that were used to estimate the diameter of the SWCNT [94]. We observed two typical SWCNT peaks located at 1,350 cm$^{-1}$ (D-band) and
1,590 cm⁻¹ (G-band). Table B1 shows experimental data for the diameter distribution of all SWCNTs synthesized in the furnace. Since the CNT growth process remained the same, we used the experimental data obtained from Appendix A to determine the diameters of the CNTs in the devices. The diameter distribution of the carbon nanotubes ranged between 1.0 nm and 2.2 nm depending on the different argon concentrations, as described in Appendix A [10]. In order to determine the carbon nanotube diameter, the Raman shift intensities were utilized and, based on the values in the table, we determined the diameter to be 1.0 nm, so that Δ1 was calculated as Δ1~0.45/d (nm) eV [112]. Contact resistance was determined by the source/drain voltage divided by the saturation current. Take the first device as an example, we obtained the contact resistance to be approximately 100 kΩ.
Figure B4. Raman spectra of the SWCNT. (A) Typical Raman spectrum of the single-wall carbon nanotube; (B) Typical radial breathing mode peaks which were used to estimate the diameter of the single-wall carbon nanotube.
Simulations were performed by Dr. Fontana’s group, using MATLAB (MathWorks, Natick, MA, USA), on the devices for different values of $V_{SD}$ and different $V_G$ variances. For the device, gate oxide thickness, $t_{ox}=300$ nm (for all devices) and we used fitting parameters $\alpha_0=0.992$, $\alpha_1=-0.05 \text{ V}^{-1}$ and $\alpha_2=0.024 \text{ V}^{-2}$. These variables are experimentally obtained, as mentioned earlier, which takes into account of graphic analysis with the slope of the characteristic curve, $V_{SD}$ value.

Figure B5 (A)–(C) shows a comparison between experimental data and modeling for $V_G$ sweeping between $-2.5$ and $+2.5$ V, $-5.0$ and $+5.0$ V, and $-10.0$ and $+10.0$ V, respectively, and for $V_{SD}$ equal to $0.03$ V, $0.02$ V, and $0.01$ V for each case. The results highlight how the gate-source voltage sweep affects hysteresis parameters $V_C$ and $w$. A larger sweep enlarges $w$ and shifts $V_C$ toward more negative values of $V_G$, while changing $V_{SD}$ does not affect these parameters. It is noted that the left segment of the curve from the model do not reach the same

<table>
<thead>
<tr>
<th>RBM bands (cm$^{-1}$)</th>
<th>Diameters (nm)</th>
<th>Relative intensity of the RBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>2.2</td>
<td>Weak</td>
</tr>
<tr>
<td>133</td>
<td>2.1</td>
<td>Medium</td>
</tr>
<tr>
<td>148</td>
<td>1.8</td>
<td>Weak</td>
</tr>
<tr>
<td>167</td>
<td>1.6</td>
<td>Medium</td>
</tr>
<tr>
<td>189</td>
<td>1.4</td>
<td>Medium</td>
</tr>
<tr>
<td>198</td>
<td>1.3</td>
<td>Weak</td>
</tr>
<tr>
<td>208</td>
<td>1.2</td>
<td>Weak</td>
</tr>
<tr>
<td>259</td>
<td>1.0</td>
<td>Strong</td>
</tr>
</tbody>
</table>

*Abbreviation: RBM, Radial Breathing Mode.*

Table B1. The diameter distribution of single-wall carbon nanotubes synthesized in the furnace.
value of the right segment of the curve on negative voltage limit. The reason for this is that, for the particular voltage sweep, the devices did not reach their maximum saturation current, and, for this, the negative voltage limit should be lower. Despite this observation and some inaccuracies due to measurement and parameter deviation, a reasonable good fitting could be observed in all graphs.

This work makes several contributions to CNTFET modeling: first, simulations with higher biases of $V_G$ were performed, whereas several prior articles that model CNTFET devices used a significantly smaller gate voltage sweep (e.g., 0 to +0.05 volts) in simulations, in comparison to our work. Secondly, it was seen that by using the adapted model, the hysteretic loop width and shift is sensitive to gate voltage bias.

In order to evaluate the accuracy of the proposed model, three other devices were experimentally tested and simulated, for $V_G$ between −10 V and +10 V, with the same procedures and conditions described earlier in this chapter. Table B2 describes the parameters used for the devices and the relative error of the comparison between the experimental and model curves. It is noted that with the results shown in Table 2, the model is applicable to other devices with different characteristics and behavior.
Figure B5. Comparison between experimental (red dot) and model (line) curves, for $V_{SD}=0.03$ V, 0.02 V, and 0.01 V. $V_G$ ranged from (a) -10 V to +10 V; (b) -5 V to +5 V; and (c) -2.5 V to +2.5 V. The variables used are the drain current ($I_{SD}$), the gate voltage ($V_G$) and the source/drain voltage ($V_{SD}$).
In conclusion, we successfully modeled $I_{SD}$–$V_G$ curves including hysteresis effects, for different voltage values and parameters, respecting the physical concepts of ballistic theory. The $L^2P$ model contributed to the characterization, as we could use its parameters to distinguish the two segments of the curve caused by hysteresis. The modeling brings detailed information about device behavior based on its characteristics.

Table B2. Comparison of parameters and relative error among tested devices. The relative error is between the modeled curve and the curve that represents the real data acquired, for each case.
APPENDIX C
FABRICATION OF POLYMERIC MICRO-CANTILEVERS FOR BIOMOLECULAR DETECTION

The micro-cantilever beam structures have been used in a variety of different applications including magnetic field sensing, bio-chemical detection, and atomic-force microscopy. In this project, a micro-cantilever is fabricated using MEMS process to ultimately detect biomolecules located on the cantilever surface.

When biomolecules attach to the cantilever beam, the mass of the cantilever beam will change, resulting in a change in the beam’s resonant frequency. By observing the change in resonant frequency, we can detect the actual binding event and confirm the presence of the biomolecules on the cantilever.

The support material for the micro-cantilever is SU-8. A piezoelectric polymer poly (vinylidene-fluoride) or PVDF layer is sandwiched by two electrodes and sit on the supporting SU-8 layer. A schematic diagram is shown in Figure C1.
PVDF is a superior piezoelectric polymer that can convert a mechanical stress into an electrical signal with great sensitivity [113]. By integrating PVDF between two metal electrodes, we can create a device that electrically measures the change in resonant frequency. And by observing the change in resonant frequency, we can detect the presence of the biomolecules on the cantilever. The preparation of the PVDF solution is given below.

1. PVDF is stored as a white powder and must be dissolved in solvent before it can be spin coated onto a substrate. The formulation of the PVDF used in the experiments corresponded to 4.0 g PVDF powder in 10 ml solution.

2. Place the organic solvent used, n-methyl pyrrolidone (NMP) in a beaker on a hotplate set to 75 °C.
3. Once the PVDF powder is weighed out and added, frequently stir the solution for 1 hour until all the powder has dissolved into a clear, viscous solution.

4. Keep the PVDF solution at 75 °C to maintain its viscosity and wait for another 1 hour to let the bubbles in solution disappear.

The micro-cantilever uses Si as substrate. A Cr layer is used as the release layer. Au/Ti is used as the electrode and adhesion layer. SU-8: 25 is used as the cantilever beam support and SU-8: 100 is used to form the big platform to strengthen the micro-cantilever device. The width and length of the beam is 100 µm and 1 mm respectively. The thickness of the beam is about 25 µm. The size of the Au electrode pads is 4 mm by 4 mm. A photo of the device is shown in Figure C2.

![Micro-cantilever diagram](image)

Figure C2. A photo of the device showing the micro-cantilever and the electrode pads

The electrode patterns are created using photolithography. Shipley MICROPOSIT S1818 positive photoresist is used to pattern the Au/Ti electrodes. S1818 is spin coated onto the metal layer at 5000 rpm for 45 seconds. The sample is then put on a hot plate at 110 °C for 1 minute for pre-exposure bake. The photoresist is exposed under UV light for 10 seconds and developed.
in CD-30 (a developer designed to dissolve unexposed Shipley photoresist) for 1 minute. Finally the sample is baked at 120 °C for 30 minutes to crosslink the photoresist.

SU-8: 25 and SU-8: 100 is also patterned using photolithography. SU-8: 25 is spin coated at 2000 rpm for 30 seconds to form a 25 µm layer. The sample is pre-exposure baked at 65 °C for 3 minutes and 95 °C for 7 minutes, exposed under UV light for 15 seconds and then post-exposure baked at 65 °C for 1 minute and 95 °C for 3 minutes. The photoresist is developed in SU-8 developer for 4 minutes after the post-exposure bake. Finally, the sample is rinsed with IPA and dried with nitrogen.

SU-8: 100 is spin coated at 3000 rpm for 30 seconds to form a 100 µm layer. The sample is pre-exposure baked at 65 °C for 10 minutes and 95 °C for 30 minutes, exposed under UV light for 35 seconds, and then post-exposure baked at 65 °C for 3 minutes and 95 °C for 10 minutes. The photoresist is developed in SU-8 developer for 10 minutes after the post-exposure bake. Finally, the sample is rinsed with IPA and dried with nitrogen.

The masks used for the top and bottom electrodes are in mirror symmetry. The mask diagrams for the electrodes and SU-8 layer are shown in Figure C3. Note that mask patterns for SU-8 is actually inversed since SU-8 is a negative photoresist.
Figure C3. Masks for top electrode, bottom electrode, SU-8: 25 support layer and SU-8: 100 platform
The fabrication of the device is carried out from top to bottom for simplicity, then releasing the completed structure from the Si substrate. The fabrication process is as follows.

1. Start with a Si substrate.

2. Deposit a Cr sacrificial layer of 100 nm.

3. A layer of 350 nm gold and 100 nm Ti is deposited and patterned.

4. Spin coat a PVDF thin film at 2000 rpm for 20 seconds to form a 2 µm thickness.
5. A layer of 70 nm Ti, 400 nm Au and 100 nm Ti is deposited and patterned.

6. The PVDF film is patterned using dry-etch. It is exposed to plasma consisting 280 sccm O\textsubscript{2} and 20 sccm SF\textsubscript{6} for 10 minutes. The top metal layer serves as the mask for the dry-etch.

7. A 25 µm layer of SU-8 is patterned onto the device.

8. A 100 µm layer of SU-8 is patterned onto the device, which excludes the cantilever beam area and serves as a structural platform.
The fabricated micro-cantilever was tested for its piezoelectric properties. The two electrodes were connected to an oscilloscope. A brief mechanical stress was applied to the micro-cantilever beam by bending it with a probe and a change in voltage was observed. The observed signal was week since the deposited PVDF film consists of an amorphous array of dipoles oriented in a random fashion. To maximize the response, the PVDF film must be poled by applying a strong electric field perpendicular to the plane of the film. This process can reorient the dipoles in one direction, producing a better response characteristic.

This device, aside from its use for biomolecular detection, can also be incorporated into a three-cantilever microsystem for health diagnostics using pulse measurements [114]. These techniques have evolved from Indian Ayurvedic and Traditional Chinese Medicine, and share common elements, including the use of the arterial wrist pulse as an indicator of health or well-
being, as illustrated in Figure C4. Furthermore, the device will be used to measure, as a proof-of-concept, the mass of a single cell [115] by determining the cantilever’s resonant frequency before and after placing the cell on the beam. Subsequent experiments would involve immobilizing antibodies on the SU-8 surface, followed by exposure to antigens against the bound antibodies. Binding events could be measured through changes in resonant frequency due to the slight differences in mass on the cantilever.

Figure C4. A photo showing the pulse diagnosis in Traditional Chinese Medicine
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