Sensor Applications of Carbon Nanotubes

by

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Abstract

A search of published research on sensing mechanisms of carbon nanotubes was performed to identify applications in which carbon nanotubes might improve on current sensor technologies, in either offering improved performance, reduced cost of manufacture, or both. Using this overview of carbon nanotube-based sensors, specific sensor technologies that could benefit from the use of newly developed techniques for producing aligned and ordered bundles of carbon nanotubes were selected.

Reports of chemical/gas, biological, optical, mechanical, and a few other sensor applications of carbon nanotubes are reviewed. Only a few of these applications might benefit from aligned and ordered bundles of carbon nanotubes. Of these potential applications, only applications in semiconducting gas sensors, DNA sensors, and infrared sensors appear to have clearly defined market niches and are sufficiently technologically mature to allow a detailed assessment of commercial potential. It is argued that DNA and infrared sensors have good commercial potential with a medium amount of risks, while gas sensors have a smaller potential. Finally, DNA sensors are believed to derive the most value from aligned and ordered bundles of carbon nanotubes.

Thesis Supervisor: Carl V. Thompson
Title: Stavros Salapatas Professor of Materials Science and Engineering

Acknowledgements

First, off I would like to give a huge thanks to Gilbert Nessim. Without his guidance, willingness to discuss different ideas, and aid in the shaping of the direction and vision of my thesis, my work would not be half its current quality; what ever it might by.

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THANK YOU!

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1. Carbon Nanotubes Overview

1.1. History

In 1991 while studying a microscopic carbon structure known as C-60, also called buckyballs, Iijima discovered a tubular microscopic carbon structure, carbon nanotubes (CNTs) [1]. These structures consist of a single layer of carbon atoms arranged in a graphite lattice and rolled into tubes that maybe capped on one or both ends. These tubes have extremely small diameters on the order of a few nanometers, and have been of great scientific interest and study due to their amazing electrical, mechanical, and thermal properties, which are greatly influenced by their size and nearly one dimensional structure.

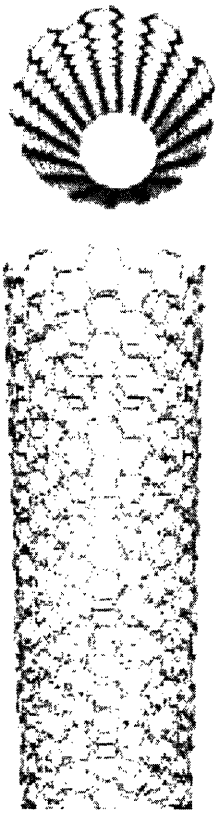


Figure 1: Computer Generated 3-D Illustration of the tip (top) and side view (bottom) of a CNT.

From: Yu, W., Xi, W., Xianggui, N. Modelling Simul. Mat. Sci. Eng. 12 (2004) 1099-1107.

1.2. Types of Carbon Nanotubes

There are several variations in carbon nanotubes that have led to the definition of a few different categories of carbon nanotubes. First, carbon nanotubes can consist of a single tube or several concentric tubes (with the diameter of each larger concentric tube increasing by ~0.35 nm over the next smaller tube) held together by surface interaction forces. A single tube is often called

a single-walled carbon nanotube (SWNT) while a group of concentric tubes is called a multi-walled carbon nanotube (MWNT). The diameter of a SWNT can vary from 0.4 nanometers to 1.4 nanometers while the diameter of a MWNT can range from a few nanometers to around 100 nanometers. One of the main differences between MWNTs and SWNTs is while MWNTs act primarily like metallic conductors (some can be semiconducting with very small band gaps), SWNTs can be both metallic conductors and semiconductors. The determining factor of the semiconducting or metallic nature of SWNTs is what is called the chirality of the carbon nanotube. The chirality can be visualized as the amount of twist in the graphite lattice when the graphene sheet is rolled and is described by two vector indices (m,n) (See Figure 2). When the indices m and n are equal the carbon nanotube is metallic, while unequal indices correspond to a semiconducting nanotube [2]. A special case of unequal indices, where n minus m is a multiple of three, yields a S-SWNT that is a sub-type of semiconductor known as a small-gap semiconductor. This leads to the actual band gap of a semiconducting SWNT depending on both the diameter and chirality of the tube.

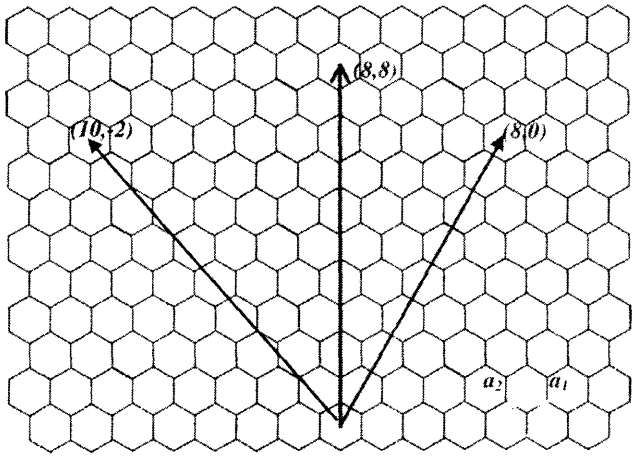


Figure 2: Graphic representation of a graphene matrix. If the sheet was rolled to allow one of the depicted vector's tail and tip to meet a SWNT with the denoted chirality would be formed. Note a_1 and a_2 are the unit vectors for m and n, respectively.

From: Dai, H. Surface Sci. 500 (2002) 218-241.

1.3. Properties and Applications of Carbon Nanotubes

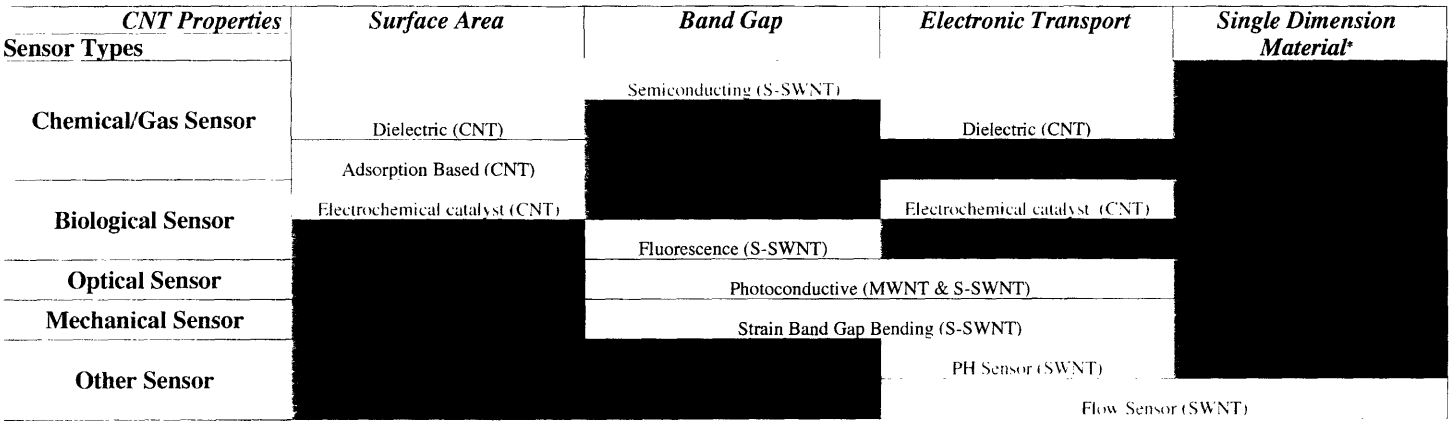
The study of CNTs has led to the discovery of many interesting carbon nanotube properties.

In fact the unusual or unique mechanical, electrical, optical, and physical characteristics provide hope that CNTs may have a large beneficial impact on many industries. Businesses are already trying to incorporate carbon nanotubes into composites to benefit from the high yield stress of nanotubes, nearly 1.2 terapascals, the most of any known material. There is hope that scanning probe microscopes will greatly benefit from SWNTs with small tip diameters and large aspect ratios (obtainable lengths of hundreds of micrometers lead to aspect ratios of above 100,000:1.) Additionally, metallic nanotubes have been shown to exhibit ballistic conduction which may lead to applications in field emission displays, integrated circuit interconnects, and other areas. Semiconducting SWNTs may provide for electronic circuits with smaller transistor sizes than possible with silicon (e. g. using CNT as a channel in a MOS-type design.) Finally, the combination of the above properties as well as high thermal conductivity, functionalization of CNTs, etc. has led many different researchers to consider the applicability of CNTs to a variety of sensing technologies.

2. Sensing Applications of Carbon Nanotubes

This wide variety of unique and interesting properties exhibited by CNTs has lead to a recent explosion in sensor research using carbon nanotubes, going from seven published papers on sensors using CNTs in 2000 to one hundred and eleven CNT sensor papers in 2004! I have found that such sensor research can mostly be broken into four main types based on the stimulus being sensed: optical, biological, chemical/gas, mechanical. Therefore, below I describe the different carbon nanotube sensor research that fits into each category. In addition there are a few sensor applications that do not fit into these categories that are described in a separate section dealing with other sensors.

Table 1: Organization and Overview of CNT-based Sensing technologies



*A single dimension material is one in which electrons have only a single axis of movement. In most materials electrons and charge can move along three axes which allow electrons to move freely in any direction within a material. Carbon nanotubes due to their extremely small diameter cause electrons to move only along the axis of the tube. This confinement to only moving forward and backwards through the tube has several interesting consequences. One of which allows flow sensing with the use of carbon nanotubes.

**The above colors represent the amount of research papers published on each sensing technology:

Green = A large body of publish papers.

Yellow = A Fair Sized body of published papers.

Orange = One or very few published papers.

2.1. Chemical/Gas Sensor Applications

Chemical and gas sensors are devices that sense simple molecules containing only a few atoms. They come in three main varieties: semiconducting, dielectric, and adsorption based.

Semiconducting gas sensors, with more than one hundred papers published on their operation, are by far the most studied sensor application of carbon nanotubes. These chemical sensors operate based on conductance changes created by charge transfer between the semiconducting single-walled carbon nanotubes (S-SWNT) and adsorbed gas molecules [3]. These S-SWNT based gas sensors operate at room temperature with high sensitivity of several hundred parts per trillion of some gases and fast response times of several seconds. However, they have very slow recovery times of around one day and suffer from a lack of selectivity due to the fact that a wide array of gases act as charge dopants.

Thankfully, there are ways to alleviate the above draw backs, if needed. To reduce sensor recovery time to under an hour, UV exposure or sensor heating can help by accelerating molecule desorption. Increased selectivity can be obtained by voltage biasing [3], palladium coating [4], and plastic coating [5]. Voltage biasing could increase selectivity to just electron donating or electron accepting molecules by effectively masking conductance changes due to the other group. Palladium coating makes the sensors selective to only hydrogen. This works by hydrogen causing palladium's work function to be reduced, allowing the palladium to donate electrons to the S-SWNT and reduce the CNT p-type doping level (S-SWNT are intrinsically p-type.) Coating the S-SWNT gas sensors with specific plastics makes the gas sensors selective to one specific molecule or a group of molecules by preventing the adsorption of other molecules through surface energy increases.

Dielectric gas sensors operate by measuring dielectric constant changes when a film of

CNTs[1] is exposed to different gas molecules. The benefit of a dielectric sensor using CNTs is that their large surface area allows greater gas adsorption for a given film volume, leading to larger changes in dielectric constant. This results in greater sensitivity. This benefit is likely common to CNTs and other nanowires, since both have large surface area to volume rations. In addition, Ong discusses how the change in conductivity of CNTs with exposure to certain gases increases the sensitivity of a particular dielectric gas sensor, a benefit not possible with other most nanowires [6].

Research on dielectric sensors is a more recent development than the previously mentioned semiconducting sensors, but seems to have caught the interest of several groups [6-9]. Each group seems to have its own method for using changes in the dielectric constant of a film of CNTs to detect gas. However, the easiest way to create a dielectric gas sensor is with a capacitor (made of two electrodes placed side by side) joined to an inductor to create an oscillating LC circuit. The capacitor is covered such that an an insulating layer is sandwiched between a film of CNTs (see figure 3). When different gases are flown over the sensor, the gas molecules are adsorbed onto the surface of CNTs in the film. If the gas molecules have a different dielectric constant than the CNT film, the capacitance for the capacitor changes, leading to a change in the oscillating frequency of the LC circuit. The gas concentration exposed to the CNT film is therefore related to the amount the LC circuit's oscillating frequency shifts by, allowing for gas sensing capabilities.

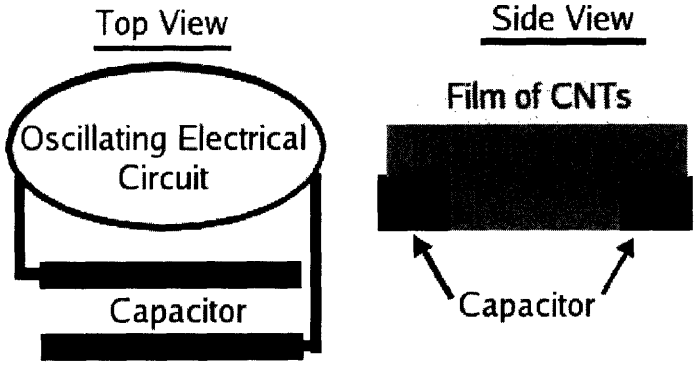


Figure 3: Illustration of a dielectric CNT gas sensor.

The greatest advantage of this type of CNT chemical sensor is the ease of design and fabrication. However the resulting change in dielectric constant, even for molecules with large

1 A film of CNTs or a CNT film is a layer of randomly oriented CNTs held together by CNT surface interactions and Van der Waal forces; it is created by depositing a solution containing dispersed CNTs on a surface and allowing the solution to dry

dipole moments, is not large enough to obtain sensitivity better than a few parts per million. E. S. snow achieved slightly better results of around one hundred parts per billion (still not as good as the above mentioned S-SWNT chemical sensors) by polarizing the CNT film with a DC field, thus increasing the dielectric change by polarizing the adsorbed gas molecules, and measuring the capacitance between the CNT film and a conductive silicon substrate with and AC current [9].

Drawbacks of dielectric gas sensors include slow recovery times of about one day and poor selectivity between molecules that change the dielectric constant in the same direction. The selectivity can be at least partly addressed with the addition of a layer of chemi-selective plastic, while the slow recovery times can be reduced the same way as in the above mentioned S-SWNT chemical sensors.

In Adsorption based gas sensors multi-walled or single-walled carbon nanotube films are place on quartz crystal microbalances[2] (QCM), surface acoustic wave (SAWs) systems, or other oscillating sensors [10-11]. When exposed to different gases, the gas molecules adsorb onto the CNT films, changing the mass of the films, and accordingly the oscillating sensors frequency changes proportionally to the change in mass. Thus, the carbon nanotube films act as molecular sponges selected for the large surface area to volume ratio of CNTs. Although, these sensors have better sensitivity than an uncoated oscillating sensors (approximately 0.1% gas concentrations) they are not nearly as sensitive as the two above mentioned gas sensor, having sensitivities of tens of parts per million. They also have slow response times of many minutes, and must be covered in chemi-selective plastic or a coated with a solution of the target gas (which increases selectivity by making it easier for the target gas to adsorb onto the CNTs, while making it more difficult for other gases to adsorb) in order to have any selectivity.

2 A Quartz Crystal Microbalance is a piezoelectric quartz crystal that is attached to an oscillating electrical circuit and uses piezoelectric properties to measure changes in mass by monitoring changes in the oscillating frequency of the crystal-electrical circuit system.

2.2. Organic/Biological Sensor Applications

Biological sensing like gas/chemical sensing is an area with large amounts of on-going research into the uses and benefits of carbon nanotubes. Such research tends to focus on two main uses of carbon nanotubes for sensing: CNTs as electrochemical catalytic amplifiers or as optical transducers.

Carbon nanotubes as electrochemical catalytic amplifiers play three slightly different roles: as plain catalysts, as catalysts and DNA anchors, and as catalysts and enzyme anchors. In the case of plain catalysts, CNT are deposited in a film on a gold or glassy carbon electrode. The CNT covered electrode and another working electrode then placed in a solution [12]. Cyclic voltammetry[3] is then performed, and the presence of a certain amount of target molecules in solution is found.

The benefits of having a CNT film over a bare electrode for electrochemical biological sensing are catalytic amplification and elimination of electrode fouling[4]. The catalytic amplification of CNTs increases the peak currents generated by target molecules during cyclic voltammetry, which improves sensitivity. The catalytic amplification also reduces the voltage at which the voltammetry induced redox reaction of target target molecules occur. Reduction of electrode fouling greatly improves the ability to reuse such sensors. Both of the above benefits can not not be performed by plain nanowires.

DNA sensing using CNTs also makes use of the catalytic amplification properties of CNTs (due to the irreversible binding of DNA at this time elimination of electrode fouling makes little

3 Cyclic Voltammetry is the process of cycling an electrical circuit through a range of voltages and measuring the resulting currents. This process is particularly used in electrochemical measurements where the cycling of voltage through electrodes in an aqueous solution causes redox reaction current peaks to appear at voltages particular to a specific chemical in solution being reduced or oxidized.

4 Electrode fouling is the chemical binding of molecules with the electrode surface causing the build up of surface impurities and the build up of molecular films on the electrode surface. This prevents the electrode from continuing to facilitate the redox reaction of additional molecules.

difference), but in addition uses the CNTs to anchor DNA markers [13]. Thus, electrodes with perpendicular or vertical arrays of CNTs are made, etched with acid to remove the caps on the ends of CNTs, and single strands of target DNA are attached to the opened tip of the CNT arrays.

The target DNA strands are selected for having series of nucleotides that are complimentary to DNA genes or other nucleotide sequences of interest to detect. The electrode with attached target DNA is then exposed to a series of solutions containing multiple DNA strands and proteins, and gently washed. If the DNA solutions contained DNA complimentary to the CNT bound target DNA, the two strands will bind together (known as hybridization) and form the usual double helix of double stranded DNA. However, if the solution does not contain any complimentary DNA the target DNA bound to the CNTs will remain as single strands. Upon performing cyclic voltammetry a different signal is generated by bound double strands of DNA than single strands of DNA, and therefore one can determine if any DNA in solutions was complimentary to the CNT bound target DNA.

One difficulty, with DNA sensors is once the DNA has bound into double helix it is difficult to return to single strands of DNA attached to CNT tips. This is an issue if the DNA sensor is to be reusable. One possible solution is to build on the research of a group from Northwestern University [14] and bathe the CNT bound DNA array in a solution highly concentrated with salt.

Biological sensing using CNT attached enzymes (the third type of electrochemical CNT sensors) also known as enzymatically functionalized CNT chemical sensors, has been pursued by several groups over the past several years [15-16], and is particularly suited for selective detection of certain chemicals in liquid solution. Most enzymatically functionalized CNT sensor research has involved the enzyme glucose oxidase attached to the tips of vertical arrays of CNTs (figure 4), though all have mentioned that the same procedures should work for other enzymes of interest.

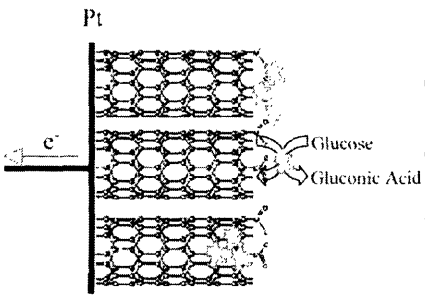


Figure 4: Illustration of CNT glucose sensor. Note how the CNTs are aligned perpendicular to the platinum electrode.

From: Sotiropoulou, S., Chaniotakis, N. Anal. Bioanal. Chem. 375 (2003) 103-105.

When solutions containing glucose are added to cuvettes holding electrodes covered with enzymatically functionalized CNTs, cyclic voltammetric measurements produce a current response that is linear to the glucose concentration down to 2.5 mM[5] of glucose. This makes such sensors more sensitive than any other electro-chemical sensors for the detection for glucose.

Biological sensing using CNTs as optical transducers seems to be a relatively small area of research, but is quite an interesting use of CNTs. In these sensors different enzymes are bound to the surface of S-SWNTs, in many cases glucose oxidase, and the covered S-SWNT are placed in solution [17]. Laser light is then used to illuminate the S-SWNT solution and the fluorescence of the S-SWNTs is detected. The way this operates as a sensor is when a target molecule is introduced into the solution, in this case glucose, the fluorescence of the S-SWNT drops linearly with the increase of the target molecules concentration. This novel sensor could provide a fast, sensitive, and repeatable way to measure concentrations of molecules in the blood in situ. However, the need for an IR laser and light detector could be costly.

5 M = Molarity a chemical unit of measure that is expressed as moles of solute per liter of solution.

2.3. Optical Sensor Applications

Optical sensing, in particular the sensing of infrared (IR) light, is another potential application of carbon nanotubes. The first paper covering the quantitative measurement of S-SWNT photoconductive response was published by A. Fujiwara [18]. In this paper Fujiwara measured photocurrent by shining an infrared laser light with oscillating optical frequency on a helium cooled SWNT film. The S-SWNT film consisted of deposited arc-discharge-produced SWNTs (diameter ~1.4 nm) and was 500 nm thick. The S-SWNT film was then contacted by two gold electrodes 10 μm apart. From measurements of this film it was noted that the photocurrent increased nearly linearly with incident light intensity up to a point, and that current responses for incident photon energies between 0.5 and 2.8 eV were greatest for photon energies of 0.7 and 1.2 eV (this matches well with the measured and expected absorption spectrum.) Also noted was an increase of the photoresponse of the film around 0.7 eV as the temperature decreased.

In addition to the possibility of S-SWNT IR detectors, the group led by L. Liu and Y. Zhang produced and tested photoconductive infrared sensors using multi-walled carbon nanotubes [19]. These sensors were produced by depositing electrodes on an oxidized silicon wafer, followed by depositing of MWNTs across the electrodes using a Langmuir Trough[6]. The Langmuir Trough through the adjustment of its

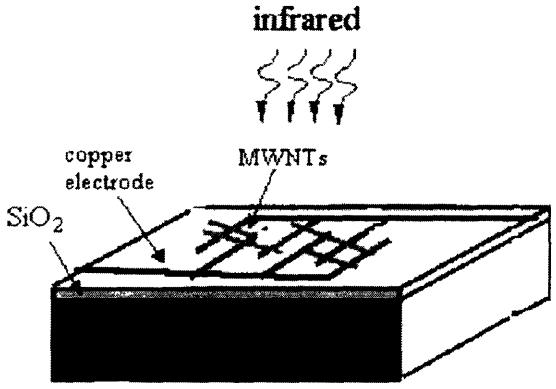


Figure 5: Illustration of MWNT IR sensor. It is show that the Langmuir Trough method, while enabling some alignment, does not place all MWNT perpendicular to the copper electrodes.

From: Liu, L., Zhang, Y. Sensors and Actuators 116 (2004) 394-397.

6 A Langmuir Trough is a machine that carefully controls the rate of transfer or deposition of a monolayer of floating material.

controls was used to align the carbon nanotubes across the electrodes (which supposedly reduced the dark current of the infrared sensors)(figure 5.) The potential advantages of carbon nanotube infrared sensors over other photoconductive infrared sensors are a more standard and perfected manufacturing processes (since much of the current silicon processes can be used), higher density sensor arrays , and improved room temperature operation.

The higher density sensor arrays would be used mostly for telescopic imaging purposes where discerning photons arriving on a focal plane nanometers apart can be important. Currently, this can not be achieved by small band gap semiconductor processes but can be achieved by quantum Well Infrared Photodetectors (both described a bit more later.)

The most questionable benefit is improved room temperature operation which was suggested to be due to reduced phonon-electron coupling in carbon nanotubes. Other papers specifically studying phonon-electron coupling in carbon nanotubes suggest that there may in fact be very strong phonon-electron coupling in carbon nanotubes. The reduction of dark current in Liu and Zhang's carbon nanotube infrared sensors would however improve room temperature operation assuming that this observation is not an error in the paper.

As for operation of the carbon nanotube infrared sensors, they did not work at first. However, the exposure to a 40V field across the Cu electrodes led to a decrease in resistance over the period of several minutes and allowed the infrared devices to operate. This was explained by the assumption that high voltages cause breakdown of the outer tubes of metallic MWNTs leaving only MWNT's with semiconducting shells. However, a paper by J. Chung suggests that all the shells of a MWNT might be removed by this voltage breakdown raising the question if the MWNT are being turned into S-SWNT before actual operation [20]. The characterization of increased conductivity with infrared light intensity involved the use of a crude heat lamp and filter system, and no specifics on the wavelengths being detected or what amount of sensitivity were included.

However, this work at least provides likely evidence that the MWNTs behave as photoconductive infrared sensors.

In conclusion, while there remains many questions to be answered about CNT photoconductivity and IR sensing, with further research, infrared sensors could prove to be a great application of carbon nanotube sensors.

2.4. Mechanical Sensor Applications

considering the amazing mechanical strength of carbon nanotubes it is quite surprisingly thatthere has been little research on mechanical sensor applications of CNTs. However, there has been some research done on the use of carbon nanotubes as stress sensors, and I speculate that carbon nanotubes could be used to create other useful mechanical sensors.

A. H. Barber demonstrated that carbon nanotubes widely dispersed in a polymer can be used to investigate polymer surface adhesion failure [21]. To be specific, Raman spectrography was used to measure the stress placed on the carbon nanotubes when surface adhesion failed. In addition, Randal Grow found that S-SWNTs placed on a silicon nitride membrane exhibit a change in conductance when the membrane is stressed by a change in pressure under the membrane [22]. This change in conductance is expected to be due to a change in the S-SWNT band-gap as the S-SWNT is bent on the deformed membrane. However, because this deformation is manifesting itself in multiple mechanisms, torsion, collapse, etc., the change in conductance does not seem to follow a predictable pattern and can not be predictably related to the stress induced in the membrane. This makes using deformation induced conductance changes inapplicable to quantitative sensing at this time.

On a more speculative note, I believe that since carbon nanotubes change resistance when they are bent, they could be used to create an artificial skin or surface movement sensor. The two challenges that must be overcome first, however, are characterizing with accuracy the resistance change with the bend angle of a CNT bundle and being able to electrically contact both ends of the vertically aligned CNT array without preventing CNT bending upon pressure application.

2.5. Other Sensing

Carbon nanotubes have been shown to perform as pH sensors [23]. However, I investigated these applications only briefly as such sensors are manufactured inexpensively and with good sensitivity using other current technologies and I do not see carbon nanotubes displacing these technologies or finding a profitable niche market of their own.

Carbon nanotubes have also been show to perform as liquid flow sensors [24]. This sensor is created simply by placing aligned single-walled carbon nanotubes across two electrodes and submersing the sensor in a liquid (figure 6). If the liquid flows in the direction of the aligned SWNT a voltage and current is generated that is logarithmically proportional to the velocity of the flow and linearly proportional the polarity of the liquid. Therefore, not only can this device operate as a flow sensor, but could be used to determine the polarity of a liquid, or even to generate power. In addition, the operation of this sensor is unique to CNTs because it depends on the one dimensional property of CNTs.

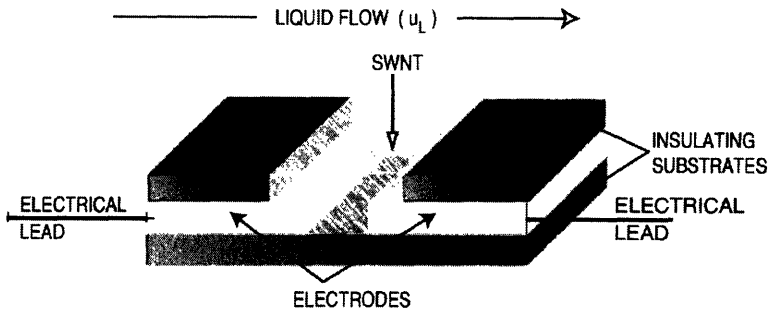


Figure 6: Illustration of a CNT flow sensor.

Ghosh, S., Sood, A. K., Ramaswamy, S., Kumar, N. Physical Review B 70 (2004) 205423.

3. Product Analysis

Now that I have covered much of the operation, advantages, and drawbacks of the whole spectrum of carbon nanotube sensors technologies, I will to focus in on the market opportunities and risks for a few of the more promising CNT technologies. Therefore, I have limited my search to sensor applications that appear (at least initially) to have promising technical attributes and appear to benefit from ordered arrays of aligned carbon nanotubes; the specific CNT production technique for which I have been asked to evaluate CNT sensor applications.

Based on these criteria, I have selected semiconducting gas/chemical sensors, photoconductive infrared sensors, and DNA sensors as the three markets I will explore and evaluate.

Just for reference, in addition to gas, DNA, and IR sensors, I have included flow and skin-like pressure sensors in the proceeding product analysis overview table. My reasoning for this is that with the emergence of a market for CNT flow sensors or the working design for skin-like CNT pressure sensors both sensors would benefit in some respects from ordered and aligned CNTs.

Table 2: The Benefit of Order and Alignment, and the Business Case for Particular CNT-Based Sensors

	Competing technology Overview	Usefulness of CNTs grown with order and alignment	Approach	Technology Advantage	Competition	Market Size (Yearly Growth)	Risk
Semiconducting Gas Sensor	-Electrochemical -Metal Oxide -Catalytic bead sensor -Chromatography -Infrared -Other CNT gas sensors	☆☆	V.A. or H.A. S-SWNT (ORD)	Sensitivity, Size, Response time, Multi-gas sensing	High	$0.5-1 billion (5-8%)	High Market Risk, Low Technical Risk
Infrared Sensor	-Thermopile -Thermoresistive -Pneumatic -Pyroelectric -Quantum Well -Small-bandgap semiconductor (HgCdTe, PbSe, etc.)	☆☆☆	V. A. MWNT (ORD)	Sensitivity, Higher temperature operation (questionable)	Average	$1.5-2 billion (unknown)	Low Market Risk, Medium-High Technical Risk
DNA Sensor	-DNA Chips -New electronic method with development process	☆☆☆☆☆	H. A. CNT (ORD)	Reduced preprocessing steps	High	$3 billion (~40%)	Low Market Risk, Medium Technical Risk
Flow Sensor	Not Available	☆☆☆	H. A. SWNT (ORD)	Not Available	Not Available	Not Available	Unknown Market Risk, Medium-Low Technical Risk
Skin-like Pressure Sensor	Not Available	☆☆☆☆☆	V. A. S-SWNT ORD	Not Available	Not Available	Not Available	Unknown Market Risk, High Technical Risk

- H. A. = Horizontally Aligned
- V. A. = Vertically Aligned
- (ORD) = Ordered CNT growth needed for multiple sensors on a chip or substrate
- ORD = Ordered CNT growth needed for sensor operation

3.1. Infrared Sensors

3.1.1. Current Technology Overview

There are two types of infrared (IR) sensing technologies: thermal and quantum.

Thermal based infrared sensors operate on the basis that infrared light generates a temperature change in any material it strikes. These sensors require any wavelengths that one does not want to detect to be filtered out by optical filters. The benefits of thermal sensors are that they are made of inexpensive materials and are easy to manufacture. Their draw backs are that they have reduced sensitivity and have fairly slow response times. Thermopiles, bolometers or thermoresistive sensors, pneumatic detectors, and pyroelectric detectors are all thermal based infrared sensors.

Quantum based infrared sensors operate by infrared photons exciting electrons from a non-conducting state to a conducting state. This method of operation occurs in semiconducting materials with low band gaps and results in fast signal response and good sensitivity. While, infrared quantum based sensors that detect wavelengths below 3 micrometers are not terribly more expensive than their thermal based counterparts, quantum based sensors that detect wavelengths above 3 micrometers are made of much more expensive materials, require more expensive manufacturing processes, and can require cooling to operate well. Most of the main quantum based far IR sensors and their operating characteristics are tabulated below.

Table 3: Operational Characteristics of Quantum-based Far-IR Sensors

	Operational Wavelengths	Optimal Operating Temperature
HgCdTe	3-15 μm	77 K
PbSe	3-4 μm	300 K
PbS	3-6 μm	77 K
Extrinsic semiconductors	10-18 μm	42 K
Quantum Well Infrared Photodetector (QWIP)	3-18 μm	77K

3.1.2. CNT Sensor Approach

Either single walled or multi-walled CNT-based optical sensing technologies could be used to make photoconductive (a sub set of quantum based) IR sensors. However to obtain far-infrared (far-IR) CNT sensors either small-gap semiconducting SWNTs or MWNTs must be used.

3.1.3. Technical Advantage

Because thermal based IR and even short wavelength quantum based IR sensors compete mainly on price, I will focus in this section only on the advantage of CNT far-IR sensors as compared to other quantum based far-IR sensors.

There are two main technical advantages of carbon nanotube far-IR sensors over other quantum far-IR sensors: operation at higher temperatures and easier manufacturing processes.

The operation at higher temperatures is a bit speculative, but supposedly, reduced phonon-electron coupling could allow sensitive room-temperature quantum IR sensing in carbon nanotubes. This is not possible in other sensors because of the large dark currents due to thermal excitation in other quantum IR sensors, which obscures any current due to IR light. However, it

should be mentioned that a few recent research papers mention that the expected reduction of phonon-electron coupling in CNTs does not exist. If this is true, the advantage of room-temperature operation would not exist.

The easier manufacturing processes of CNT-based IR sensors is a more definite advantage than room temperature operation. This stems from the fact that other quantum based far-IR sensors are made out of unusual metal-semiconductor ternary systems. Therefore, the manufacture of sensors from these ternary systems require unique manufacturing equipment. In addition, the most popular quantum far-IR sensor uses mercury as a component, likely adding stringent processes to comply with Environmental Protection Agency (EPA) mandates. CNT based far- IR sensors on the other hand would be manufactured using CVD and, likely, conventional processes and equipment developed for Si technology. This should allow the CNT sensors to be manufacture faster, in larger batches, and with higher yield likely making them cost competitive, or even cheaper than other far-IR sensors.

3.1.4. Market and Competitors

3.1.4.1. Market:

The market for IR sensors is quite varied due to the many applications for which they have been found useful. IR sensors are used extensively in fiber optic communication and data systems, in which IR light is the propagating wavelength. They are used in some chemical and biological detectors due to low tissue absorption and fluorescence and the ability to recognize some chemicals based on their absorption spectra. In addition, IR sensors are used in short range wireless communication, in night vision goggles, on telescopes and satellites, and many more application areas.

The area of the IR sensor market I believe to offer the best chance for CNT IR sensors to gain a market foothold is military and high resolution telescope applications. These two market areas make extensive use of quantum-based far-IR sensors for high sensitivity imaging, vision, and tracking applications. The CNT-based far-IR sensors could therefore compete in these markets where, despite the low volumes, they are likely to have a price advantage over the competition. For example, the price Cal Sensors charges for PbS sensors, a would be far-IR competitor with CNTs, sells a single far-IR sensor for approximately $500 and charges $2000+ for a 256 element two dimensional array of far IR sensors.

However, to operate in this market (where performance is king) CNT must show that they can obtain, at worst, the same sensitivities and operating temperatures of today's better quantum based IR sensors to then compete on price.

3.1.4.2. Market Size:

In "Study on Temperature Sensors in the Americas" by Ducker Research Company, Inc., concluded that the market size for temperature sensors is $540 million. Additionally, revenues for the North American infrared gas sensor market totaled $70 million in 2004. Based on these two numbers and the fact that there are quite a few other markets I would guess that the market for all IR sensors is approximately 1.5 to 2 billion dollars. (I couldn't find enough information to estimate the growth of the IR sensor market.)

3.1.4.3. IR Detector Manufacturers:

a) Thermal

Servo Corporation of America - Based in New York, thermistor & pyroelectric devices, as well as products in other areas such as radio navigation

InfraTec - German Company, pyroelectric devices

IR Microsystems - German Company, pyroelectric devices, sole business

Dexter Research Center - Based in Michigan, thermopile, sole business (includes filters and optics for spectrum selection)

BAE Systems - International, Pyroelectric, sells many other products

PerkinElmer, Inc. - Based in Germany, thermopiles (major producer), other produces in health and life sciences

b) Quantum

Cal Sensors - Based in California, founded in 1986, PbS and PbSe devices.

Vigo Systems Ltd. - Polish Company, HgCdTe devices (uncooled and Cooled)

3.1.4.4. IR Detector Customers:

Customers for IR sensors are varied just like the market for them. Most thermal-based and some short-wavelength IR sensors are sold to distributors like Electro Optical Components Inc. who then sell them to end customers. However, customers with large IR sensor needs or those buying far-IR sensors quite often buy directly from the manufacturer.

3.1.5. Risks

The two main risks of entering the far-IR market with CNT sensors are the small size of the market and the need for further research and technical clarification.

The small market size is a problem due to the low quantities of CNT sensors that would be manufactured and sold each year. This limits the mass manufacturing benefits of CVD growth and silicon based manufacturing processes.

The need for further research and technical clarification stems from the fact that the single paper published MWNT IR sensor appears to only be a cursory look at MWNT's IR sensing abilities. This leave it open to speculation whether the claimed dark current benefits of aligned MWNT, the operation at higher temperatures without sensitivity loss, and the claimed detection of far-IR wavelengths are valid results. Only further experiments and tests can verify the validity of the claimed results.

3.1.6. Sensor Benefits of Ordered and Aligned CNTs

CNT IR sensors would benefit from ordered aligned CNTs in two ways: aligned CNTs supposedly reduce the dark current of CNT far-IR sensors and ordered bundles horizontally grown CNTs could allow for faster and easier manufacture of IR sensor arrays.

The reduced dark current allowed by aligned CNTs, if true, would play a large role in achieving increased sensitivity and improved room temperature operation. This could play a significant role in allowing higher feasible product prices, either increasing profit or facilitating faster market penetration at lower prices.

Ordered horizontally grown CNTs may be of benefit by allowing an array of CNT IR sensors to be easily manufactured. Laying the horizontally grown CNTs on a substrate while still

separated by alumina, would allow the deposition and ion etching of two long electrode strips perpendicular to the CNTs to create a long line of IR Sensors (with each sensor consisting of aligned CNTs parallel to the alumina separators and electrodes on either end of the aligned CNTs.)

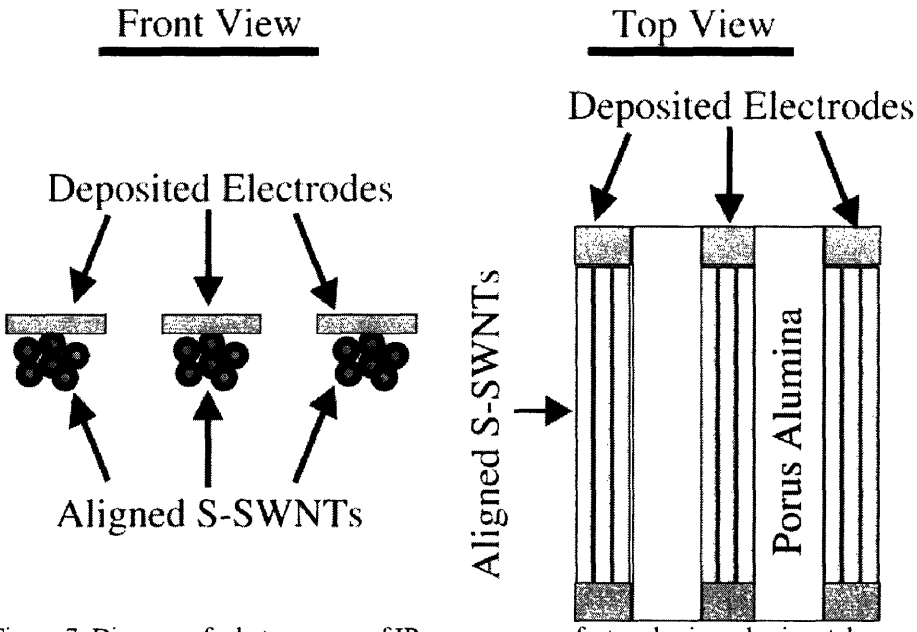


Figure 7: Diagram of what an array of IR sensors, manufactured using a horizontal ordered array of CNTs, would look like.

3.2. Gas Sensors

3.2.1. Current Technology Overview

The variety of different gas sensors available to those with gas detection and monitoring needs is nearly endless and an entire technical report could probably be devoted just to describing the different methods of gas sensing. However, only a handful of gas sensing technologies are used in a majority of gas sensors currently being sold. Therefore, I will describe the three main gas sensing technologies, as well as two others that are of use in high sensitivity gas detection.

First, possibly the most common and oldest gas sensing technology is the electrochemical gas sensor. These sensors work through a reaction occurring between the target gas and a specified in-solution electrolyte. The reaction generates a voltage across electrodes, and the voltage is normally proportional to the concentration of the gas being sensed. These sensors are usually a few millimeters in size. Due to its chemical nature, this sensor become less reactive over time, as the sensing electrolyte breaks down or becomes bound to different molecules, requiring the sensor to be recalibrated and eventually replaced.

Another popular gas sensor is the solid state or metal oxide semiconductor gas sensor. This sensor detects gases based on gas molecules adsorbing on the sensor surface and causing a resistance change that decreases with increasing gas concentrations and is non-linear. One drawback, is that many gases induce this resistance change, requiring the addition of a gas selective plastic covering or other filter mechanism. These aren't available for all gases and aren't always selective for detection of a specific gas. The advantages of this type of sensor are sensitivity down to parts per million (PPM), sizes as small as several micrometers, and the lack of

chemical breakdown, which allows only occasional recalibration to correct for drifts in the resistance to expected at a know gas concentration (this concentration is used as reference point to calculate the expected resistances for other gas concentrations.)

Next, a gas sensor called a catalytic bead sensor is used quite often for combustible gas detection and can be as small as a few millimeters. This sensor is created by placing a reference and sensing wire in a Wheatstone Bridge circuit. The reference wire is a simple metal wire with a small amount of its surface area coated with glass shell, while the sensing wire is has a small amount of its surface area coated with a particular catalyst encapsulated in a shell of platinum. When the catalyst-coated wire is exposed to a certain minimum amount of a target combustible gas (this amount depends on the gas and catalyst), the catalyst causes a combustion reaction inside the platinum bead. This heats the wire, expanding it, and thereby changing the conductivity of the wire. This conductivity change is positive and linear up to a point; usually well above the amount needed to cause an explosion in the case of an igniting event. Past this point a false negative reading appears on the gas sensing meter. This sensor, similar to the electrochemical gas sensors, is based on the chemical operation of a catalyst which makes the sensor gas specific, but requires recalibration and replacement. While the 0.1% or so minimum gas sensitivity isn't very good, it is more than enough for explosive gas detection since combustion will not normally occur below several percent.

When gas concentrations of several parts per billion or lower are to be detected, one type of sensor usually used is a gas chromatography detector. This detector is quite large, usually several tens of meters tall due to the need for a long furnace heated tube. Gas chromatography sensors operate by injecting a gas into a chamber and varying the temperature of the chamber, causing the components of the gas to rise through a large tube at different temperatures. Derivatives of a plain gas chromatographer use a flame (flame-ionization detector) or light (photoionization detector) to

ionize the gases rising through the detector tube and allow detection at electrodes at the top of the tube. These sensors, while having high sensitivity, sometimes cannot detect the exact gas makeup (instead giving several possibilities) and, due to the injection process and detection time, aren't useful for gas safety detection. Therefore, these sensors are used mainly in analyzing gas output of manufacturing processes and determining environmental compliance for gases that can only be emitted in trace amounts.

The largely available, high sensitivity gas detectors, are IR spectrography sensors. These sensors, pass IR light through a gas and then detect the light with a detection panel. The light detector determines how much IR light has been absorbed at different wavelengths and, based on this absorption spectrum determines, the type and amount of gas present. This analysis depends on knowing the majority carrier of the gas, which in most cases is not a problem. IR sensors are starting to replace ionization detectors for high sensitivity applications and in some cases are even replacing gas sensors with average sensitivity. This is due to their high sensitivity, high selectivity, and real time operation, in addition to their shrinking size (the smallest of theses sensors now a day can be several centimeters in size.)

3.2.2. CNT Sensor Approach

The CNT sensor approach is to use the semiconducting gas sensor approach described previously.

3.2.3. Technical Advantage

The advantages of CNT semiconducting gas sensors are size, sensitivity, and the possible ability to assess the composition of complex gas mixtures, and fast response times.

The size advantage is obvious. A single S-SWNT is enough to create a CNT gas sensor, though multiple CNTs are preferred from a yield perspective, thereby making the theoretically smallest CNT gas sensor around 10-20 nm (the length of a short nanotube.) This obviously makes the electrode contact and sensor mounting substrate size the limiting factor in how small a gas sensor one can achieve.

The sensitivity of CNT gas sensors is good enough to detect a few hundred parts per trillion (PPT) of some gases making it more sensitive than all other sensing methods except for IR spectrography sensing. This sensitivity cannot be obtained for all gases, but parts per billion (PPB) sensitivity can be obtained for a large variety of gases.

Finally, the ability to detect multiple gases by applying different chemoselective plastic to parallel CNT gas sensors on a single mounting substrate allows for accurate determination of the make up of a complex mixture of gases. This could be especially useful in cutting-edge manufacturing processes where the input of multiple materials or gases must be extremely carefully controlled.

The response times of semiconducting gas sensors on the order of several seconds greatly beats that of other sensor which usually take at least a minute to detect a signal, and may make semiconducting CNT gas sensors the future sensor of choice when immediate warnings are necessary. For example, sensors meant to detect extremely toxic gases to provide immediate safety warnings would likely choose CNT sensors, if available, for their fast respone with little regard for their higher cost.

3.2.4. Market and Competitors

3.2.4.1. Market:

As mentioned in a Frost and Sullivan report [25] most gas sensing technologies have been around for quite a long time and therefore the market has trended towards becoming a commodity market. Multi-gas sensors and possibly highly specialized sensors are the two areas where I would foresee commodity pricing becoming the norm in the near future. This is due to continued development in these two areas. However, due to the high cost of multi-gas sensors, most customers will purchase single gas sensors for their needs.

Therefore, I suspect that CNT sensors would perform best in the small markets for high sensitivity process-control multi-gas sensors, chemical-warfare sensors (I'm assuming some of these chemicals are deadly in very small amounts), real-time EPA compliant sensors, or other high-sensitivity gas detection markets, especially where size and the ability to sense complex gas mixtures might matter.

3.2.4.2. Market Size:

I searched freely available reports, the annual industry accounts section of the US Department of Commerce: Bureau of Economic Analysis (www.bea.doc.gov/bea/dn2/home/annual_industry.htm), and annual reports of gas sensor manufacturers (especially their market and competition sections)[26-28] for gas sensor market information. However, I could not find any market size and growth information. Short of paying $4000 for a gas sensor market report, I decided to go with the next best thing, estimation based on sensor manufacturers' revenue. Considering Industrial Scientific Corporation is the largest gas sensor manufacture I found, by far, I decided to base my market estimate on their revenues. First, I

took 1995-1998 revenues to estimate an average amount of market growth per year. This came to between 5-8% yearly market growth; reasonable for a fairly mature market. Next, I applied this to their 1998 revenues and came up with estimated 2005 revenues for Industrial Scientific Corporation of around $100 million. Finally, assuming they have a 10-20% market share of the entire gas sensor market (roughly based on the amount a of market share obtained by a typical large player in a diverse market), the entire market for gas sensors is between $0.5-1 billion yearly. I think it is also reasonable to assume that the gas sensor market is still growing at 5-8% per year.

3.2.4.3. Gas Sensor Manufactures:

Below is just a small listing of the many players in the gas sensing market, most of which are private companies, very small pure sensor manufacturers, or fairly large corporations who have a small division devoted to gas sensor manufacturing. The only fairly large, pure gas sensor manufacturing company I could find information on was Industrial Scientific Corporation, which was a public company until 1998 and then went private.

Air Instruments, Applied Sensors, Bacharach Instruments, Bio Systems, Comag IR, Draeger Safety Inc., e2V-Technologies, General monitors, Industrial Scientific Corporation, American Sensors Inc., Optical Sensors Inc., Fiberchem Inc., Thermo Instrument Systems, and Mine Safety Appliances Company, and RAE Systems Inc.

3.2.4.4. Gas Sensor Consumers:

Mostly businesses with dangerous working areas or companies that need to monitor manufacturing processes or EPA standard outputs.

3.2.5. Risks

I believe that the main risk to the success of CNT semiconducting gas sensors is the small market opportunity.

The problem with the size of the gas sensor market is, if a business is forced to focus on a small niche, at most it could support a few employees. This is makes it especially hard to justify the large manufacturing start-up costs to produce CNT gas sensors, as there would be little expected return on investment.

3.2.6. Sensor Benefits of Ordered and Aligned CNTs

Unfortunately, Gas sensors do not gain any advantage from being aligned versus randomly oriented. Nor does a single gas sensor gain an advantage from an ordered set of carbon nanotubes. However, any ordered array of aligned S-SWNTs would likely benefit the creation of multi-gas sensors. This benefit derives from the benefit of horizontally or vertically ordered carbon nanotubes to create a parallel array of gas sensors, analogous to the manufacture of parallel arrays of IR sensors. In addition, an ordered array of gas sensor might make it possible to use a modified lithographic method to individually functionalize or coat CNT gas sensors with the necessary different chemoselective plastics that would be necessary to create multi-gas sensors.

3.3. DNA Sensors

3.3.1. Current Technology Overview

There is currently one main method for DNA sensing and one potential technology is being developed.

The current main method for DNA sensing is simply to see whether unknown DNA sequences bind to known DNA sequences using fluorescence. Basically one creates a target DNA sequence by placing known DNA nucleotides in a desired pattern. This target DNA is then bound to a glass chip. At the same time DNA extracted from a human cell or other source is chemically bound to a group of specific molecules that fluoresce when illuminated with laser light. A solution containing fluorescently functionalized DNA is then poured on the glass chip, the glass chip is cleaned, and a laser light is shown on the glass chip. If a machine detects the chip fluorescing, then it is know that some of the extracted DNA is complementary to the know DNA sequence on the chip. This is because only complementary DNA sequences bind together; therefore washing will remove all fluorescently functionalized DNA that is not bound to target DNA on the glass chip.

It must be noted that extracted DNA must first be replicated many times using a polymerase chain reaction (PCR) method, before being fluorescently bound and placed on a chip. This is because the amount of DNA that would normally be present is not enough to generate the minimum amount of fluorescence a detector can recognize.

Current DNA chips detect many DNA sequences in a single test by placing a grid of different known DNA sequences on a glass chip. Therefore, any areas that fluoresce when illuminated by a laser correspond to known complimentary sequences in the human or other DNA.

The technology being developed eliminates the need for replicating the extracted DNA. In this technology, target DNA sequences are laid across pairs of electrodes located on a glass chip [14]. Gold nanoparticles are then bound to extracted DNA and a solution containing the extracted DNA is poured on the DNA and electrode-covered chips. After, allowing time for DNA hybridization, the chips are washed and a developing technique, similar to that of film development, places silver particles around any gold nanoparticles attached to hybridized DNA. Finally, electrical current flow occurs between electrodes bridged by the silver particles.

3.3.2. CNT Sensor Approach

The CNT DNA sensor approach is the approach described previously where DNA is bound to CNTs and cyclic voltammetry is performed to detect hybridization.

3.3.3. Technical Advantage

The advantage of a CNT DNA sensor is that the need for extracted DNA replication, and extracted DNA fluorescence labeling or gold particle labeling could be eliminated.

First, DNA replication could be eliminated due to the CNTs increasing the current signal generated cyclic voltammetry enough to detect even the small amount of DNA produced by extraction. This is great because DNA replication can be a time consuming and expensive process.

On the other hand, DNA labeling is eliminated because, when extracted DNA binds to the CNT-attached DNA targets, the cyclic voltammetry peaks are reduce due to DNA binding (also

known as hybridization). The change in signal can be further increased by gently washing the CNT DNA sensor and adding an enzyme solution that binds to unpaired target DNA generating a completely different signal in these areas. In addition to creating savings on DNA labels, this benefit of CNT DNA sensors also eliminates the time needed to label extracted DNA.

3.3.4. Market and Competitors

3.3.4.1. Market:

The current market focuses mainly on customers doing research on mapping different organism genomes (all the DNA that controls the make-up of a single species) or discovering what gene variations occur within a particular species. However, with the elimination of the need for DNA labeling and amplification, DNA sensors might be used for biological warfare detection. At the right price point, DNA sensors would likely be purchased by medical offices to do certain in-house disease detection and diagnosis.

In addition, the demand for DNA sequences and the complexity of most DNA chips leads to very high chip prices. For example, Affymetirics Inc. in 2002 introduced a chip that could detect 500 different DNA sequences that at the time cost $12,000 [29]. Considering that these chips are one use, disposable chips, it is quite amazing that they sell.

Therefore, CNT DNA sensors, despite the high difficulty and expense of CNT growth, should be able to compete in the current DNA chip market due to their elimination of preprocessing steps and the high prices of other DNA chips. In addition, CNT DNA sensor by removing preprocessing steps could become the only DNA technology able to detect biological warfare agents in the field (though a preprocessing step to break extracted DNA into smaller pieces would be a necessary preprocessing step.) This could be quite a great entry market due the

military's low price sensitivity and the increasing threat of other terrorists and militaries having biological weapons.

Note: Medical office purchase of CNT DNA chips is a market that despite potential, would require development of a fairly inexpensive manufacturing process. While CNT sensors eliminate steps needed to do DNA sensing, thereby reducing cost and greatly speeding up test times, they are still likely to be too expensive for medical offices to conduct single-use tests with. Also, extensive reliability testing of CNT DNA chips would be needed before being offered to medical office. This is necessary, to avoid the potential for expensive law suits and other litigation.

3.3.4.2. Market Size:

According to a report by Dooley the global market for DNA chips (also know as genomic microarrays) was expected to be $2.1 billion by 2004, with an annual growth rate of approximately 40% [29]. The reason for this explosive growth rate is that scientists have only decoded the genome of the smallest fraction of know species. In fact, the entire genome is known for less than one hundred of the 2 million or so currently known species. Not only does this leave an incredible number of genomes to explore and decode, with in any particular species the genes of each individual vary and the decoding of theses variances is an important step in discovering the cause and possible fix of many genetic diseases.

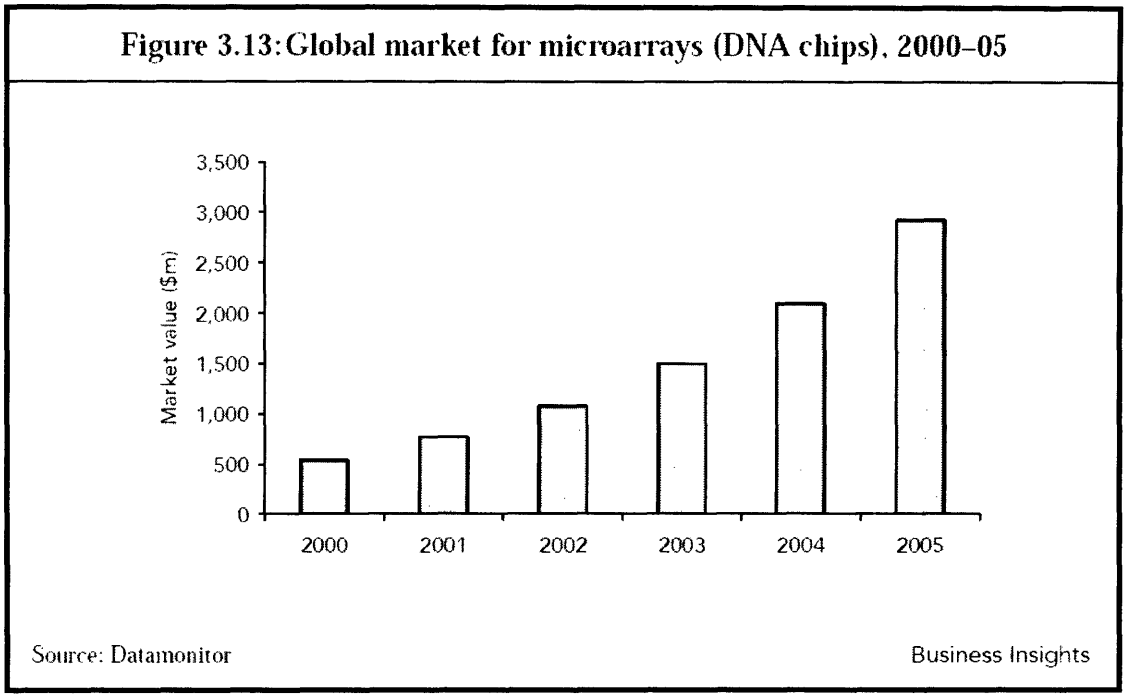


Figure 8: Predicted global market for DNA chips from 2000-2005.

From: "The Genomics Outlook To 2005" Business Insights Ltd. 2002.

The largest manufacturer of DNA chips is Affymetirics Inc. with revenues of $330 million in 2004, or approximately 15% of the global market. This suggest that the market is not dominated by any single corporation, leading to the likely hood that it is highly competitive.

3.3.4.3. DNA Chip Manufacturers:

Below are just some of the manufacturers in the fast growing market for DNA chips.

Affymetirics Inc., Applied Biosystems, Inc., BD Biosciences Clonetech, CombiMatrix Corporation, Digital Gene Technologies, Illumina, Inc., Lynx Therapeutics, Inc., Nanogen, Inc., Visible Genetics Inc. (a subsidy of Bayer), Celera Genomics Group of Applera, Rosetta Inpharmatics (Merck), Curagen, deCODE Genetics, SEQUENOM, Gemini Genomics, Human Genome Science, Exelixis, and Caliper Technologies

3.3.4.4. DNA Chip Consumers:

Medical Research Groups, Bioengineering Firms, Genetic Science Research Labs, Medical Practice Offices (future), and Military (Biological Warfare Detection) (future)

3.3.5. Risks

The risks of this technology are mainly technological with some slight economic problems.

The main technological hurdle that must be overcome is whether multiple DNA sequences can be detected in a single sensor cell. The reason this is a problem is that cyclic voltammetry method used in the functioning of CNT DNA sensors detects chemicals given off by single strands of DNA that are reduced when a complimentary strand of DNA is bound to it. If these chemicals would interfere with cyclic voltammetry measurements of adjacent target DNA detectors then a way to chemically isolate each group of vertical CNTs with different target DNA would be necessary. This is could prove difficult to do in a liquid solution where diffusion of reactive species could disrupt nearby CNT groups. This would greatly limit the applicability of a CNT DNA sensor.

The main economic problem that must be addressed before starting a CNT DNA sensor manufacturing business is that sensors are not reusable. Therefore, the CNT sensor could solely add value above other DNA chips based on the value of the time and equipment saved by eliminating amplification and labeling; and in the case of the new DNA technology described above, only on time saved by eliminating labeling. However, it is likely that CNT DNA sensors could eventually detect many more DNA sequences on a single chip than other DNA sensors, owing to the small size of CNT tips, resulting in a small binding area for DNA sequences, and the limit to how small an area can be defined for DNA binding with current DNA chip technology.

3.3.6. Sensor Benefits of Ordered and Aligned CNTs

Carbon nanotube DNA sensors benefit the most from ordered and aligned CNTs.

First, vertically aligned CNTs are a necessity for maximum CNT DNA sensor sensitivity. This is due to the DNA attachment process occurring only at the open end of a CNT. Therefore, if the CNTs were not aligned perpendicular to the base electrode many of their tips would be hidden in a film and less than optimal DNA loading would occur.

Second, having order aligned bundles of CNTs where the bundles have a know area of exposed tips would allow the maximum sensitivity to be know for all such DNA sensors. This is because the sensitivity of is proportional to the DNA loading which is proportional to the area of exposed tips.

Finally, if CNT DNA chips are to detect many DNA sequences in parallel, just as Affymetirics' DNA chips do, then a way of separately functionalizing each DNA bundle must be devised. I'm confident that the positional knowledge that ordered vertical CNT arrays offer will be greatly beneficial in this task.

3.4. Conclusion

In conclusion, there are quite a few avenues open for research on sensing applications of carbon nanotubes. While they may not be as promising as other applications of carbon nanotubes, sensor applications may be closer to producing marketable goods than most other carbon nanotube applications. In fact, in many cases the question of market potential is much larger than that of technical and manufacturing feasibility.

Along this line, I would suggest CNT DNA sensors as the CNT sensing technology with the largest potential. Despite several technological hurdles in the way of achieving a final product, I feel that CNT DNA sensors have the best balance of both benefiting from aligned and ordered CNTs and appearing to have a good market potential. IR sensors and Flow sensors would be my runner up choices because they appear to make the most use of unique and interesting CNT properties, however they exhibit much more problems and have smaller markets then DNA chips.

In my opinion, the best continuation of this research on CNT sensors would be to pick one of the CNT sensor technologies explored and delve deeper into the market conditions of that particular sensor. This would be especially interesting if a hypothetical manufacturing process was developed and then analyzed for feasibility using a cost model and utility analysis. This could lead to the identification of where current CNT growth and processing methods shine, as well as where research could most improve on current processes. The best thing about CNT sensors is they are an application of CNTs that is not hugely theoretical, but can be played with in today's labs!

References

[1] Iijima, S. "Helical microtubules of graphitic carbon." Nature 354 (1991) 56–58.

[2] Dai, H. "Carbon nanotubes: opportunities and challenges." Surface Science 500 (2002) 218-241.

[3] Kong, J, et. al. "Nanotube Molecular Wires as Chemical Sensors." Science 287 (2000) 622-625.

[4] Sayago, I. et al. "Hydrogen sensors based on carbon nanotubes thin films." Synthetic Metals 148 (2005) 15-19.

[5] Qi, P. et. al. "Toward Large Arrays of Multiplex Functionalized Carbon Nanotube Sensors for Highly Sensitive and Selective Molecular Detection." Nano Letters 3.3 (2003) 347-351.

[6] Ong, K., Zeng, K., Grimes, C. "A Wireless, Passive Carbon Nanotube-Based Gas Sensor." IEEE Sensors Journal 2.2 (2002) 82-88.

[7] Chopra, S. et. al. "Selective gas detection using a carbon nanotube sensor." Applied Physics Letters 83 (2003) 2280-2282.

[8] Langlet, R. et. al. 2004. "Influence of molecular adsorption on the dielectric properties of a single wall nanotube: A model sensor." Journal of Chemical Physics 121 (2004) 9655-9665.

[9] Snow, E. S. et. al. "Chemical Detection with a Single-Walled Carbon Nanotube Capacitor." Science 307 (2005) 1942-1945.

[10] Penza, M. et. al. 2004. "Alcohol detection using carbon nanotubes acoustic and optical sensors." Applied Physics Letters 85 (2004) 2379-2381.

[11] Penza, M. et. al. "Carbon nanotubes-based surface acoustic waves oscillating sensor for vapor detection." Thin Solid Films 472 (2005) 246-252.

[12] Gong, K. et. al. "Novel electrochemical method for sensitive determination of homocysteine with carbon nanotube-based electrodes." Biosensors and Bioelectronics 20 (2004) 253-259.

[13] Kerman, K. et. al. "Escherichia coli single-strand binding protein-DNA interactions on carbon nanotube-modified electrodes from a label-free electrochemical hybridization sensor." Analytical Bioanalytical Chemistry 381 (2005) 1114-1121.

[14] Park, S. et. al. "Array-based electrical detection of DNA with nanoparticle probes." Science 295 (2002) 1503-1506.

[15] Loh, K., Zhao, S., Zhang, W. "Diamond and carbon nanotube glucose sensors based on electropolymerization." Diamond and Related Materials 13 (2004) 1075-1079.

[16] Sotiropoulou, S., Chaniotakis, N. "Carbon nanotube array-based biosensor." Analytical Bioanalytical Chemistry 375 (2003) 103-105.

[17] Barone, P. et. al. 2004. "Near-Infrared optical sensors based on single-walled carbon nanotubes." Nature Materials 4 (2005) 86-92.

[18] Fujiwara, A. et. al. "Photoconductivity in Semiconducting Single-Walled Carbon Nanotubes." Japan Society of Applied Physics 40 (2001) L1229-L1231.

[19] Liu, L., Zhang, Y. "Multi-wall carbon nanotube as a new infrared detected material." Sensors and Actuators 116 (2004) 394-397.

[20] Chung, J. et. al. "Multi-walled carbon nanotubes experiencing electrical breakdown as gas sensors." Nanotechnology 15 (2004) 1596-1602.

[21] Barber, A. H. et. al. "Characterization of E-glass–polypropylene interfaces using carbon nanotubes as strain sensors." Composites Science and Technology 64 (2004) 1915-1919.

[22] Grow, R. et. al. "Piezoresistance of carbon nanotubes on deformable thin-film membranes." Applied Physics Letters 86 (2005) 093104.

[23] Xu, Z. et. al. "Single-wall carbon nanotube-based voltammetric sensor and biosensor." Biosensors and Bioelectronics 20 (2004) 579-584.

[24] Ghosh, S., Sood, A. K., Kumar, N. "Carbon Nanotube Flow Sensors." Science 299 (2003) 1042-1044.

[25] "North American Gas Sensors and Gas Analyzers Markets." Frost and Sullivan 24 Mar 2004: Executive Summary.

[26] 1998 10-K. Industrial Scientific Corporation.

[27] 2005 10-K. Mine Safety Appliances Company.

[28] 2005 10-K. RAE Systems Inc.

[29] Dooley, J. "The Genomics Outlook To 2005: Transforming pharmaceutical and diagnostic markets." Business Insights Ltd. 2002.

Appendix A – IR Sensor Patent Discussion

In searching for an blocking patents on infrared carbon nanotube sensors, I performed searches for any patent abstracts, both issued and pending, that contained the words carbon nanotube or infrared. I then scanned through the results eliminating any patents whews' titles did not suggest they had anything to do with infrared sensors or the manufacture of aligned CNTs. Finally, of all the patents that seemed to have titles and abstracts pertinent to the manufacture of CNT infrared sensors, I carefully read the claim to eliminate any who's claims were too specific to be infringed. This left me with three possible blocking patents for the manufacture of CNT infrared sensors.

The first patent, 4,795,907, was filed on January 1989 and is held by Fujitsu Limited. This patent describes an infrared sensor based composed of an optical filter an absorbing substrate and a conductive electrode. However, the conducting electrode is specifically mentioned to cover the entire absorbing substrate except for small optical opening. This is not the case with a carbon nanotube infrared sensor which only has small electrodes attached to either end of the carbon nanotubes, which prevent the above patent from applying to said technology.

The second patent, 5,006,711, was filed in April 1991 by Fujitsu Limited as well. This patent covers any two dimensional array of infrared detectors with electrical connections. Unless a license for this patent is obtained, this patent would definitely prevent the manufacture of imaging arrays or focal planes until after 2011.

The final patent, 6,129,901, was filed in 1996 and covers the growth of vertically aligned carbon nanotubes by CVD. This patent would definitely have to be licensed in some respect as we do not have plans to use any other method to grow the carbon nanotubes to produce infrared sensors. One possibility would be to purchase aligned carbon nanotubes, but this is unlikely as we would like to grow the carbon nanotubes on an already deposited electrode.

Appendix B – Journal Article Summaries

1.

Single Walled Carbon Nanotube Thin-Film Sensor for Ultrasensitive Gas Detection

Wongwiriyapan, W. et. al.	2005	Jap. Journal of App. Physics
Chemical Sensing - NO_2 and Cl_2	SWNT	semiconducting
High Sensitivity - ppb	Semi-Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

according to the air quality standard NO_2 is required to have a concentration lower than 40 ppb; difficult to do with conventional gas sensors.

- Device is made by growing (CVD with Fe catalyst) SWNT thin film (CVD with Fe catalyst) on Al_2O_3 substrated between interdigitated Pt electrodes, with heater under SWNT film.
- Constant 100 mV as used to detect change in conductance as molecules adsorbed.
- Conductance changed due to adsorption doping of semiconducting SWNT even though both metallic and semiconducting SWNT were present in the film.
- The sensors detected down to 50 ppb of Cl_2 and NO_2 in 160s and were returned to initial conductance due to deadsorption of gas using a heater.
- Electrical breakdown of SWNts increased initial resistance, leading to increased sensitivity and likely ability repeatably achieve the same initial resistance over all devices.

2.

Nanotube film based on single-wall carbon nanotubes for strain sensing

Dharap, P. et. al.	2004	Nanotechnology
Mechanical Sensing	SWNT	resistivity change
Good Sensitivity?	Selective	Reusable w/ some measurement variation, Unknown Reproducibility
Response:	Market:	Mfg:

- A thin film of randomly oriented CNT and DMF composite was used with a 4 point probe to create a strain sensor.
- The two outer probe points generated a current through the film and a voltage was then measured by the two inner probe points
- When the film was applied to a copper sheet that under went cyclical tension and compression stressing, the voltage measured by the 4- point probe varied linearly with the strain and stress of the copper sheet.
- Electrical contact of and current flow in the CNT film seems like it could be problematic, but this paper does not mention any such problems and causes me to be a bit skeptical

about their results.

- Otherwise this paper suggest a useful sensor for "multidirectional and multiple location strain sensing on the macro scale."
- Most of the voltage change in the CNT film is due to CNT resistivity change and not a change in the dimension of the film.

3.

Single molecule detection and macromolecular weighing using an all-carbon-nanotube nanoelectromechanical sensor

Roman, C., Ciontu, F., Courtois, B.	2004	IEEE Conference on Nanotechnology
Biological Sensing	SWNT	oscillation frequency change
Best Possible Sensitivity	Selective	Reusuablility Unkown, Probable Reproducibility
Response:	Market:	Mfg:

- The proposed sensor to do single molecule detection is a carbon nanotube cantilever stabilized in the vertical direction by a carbon nanotube baring. The cantilevered CNT is then oscillated horizontally across the baring. The oscillation frequency would change if a molecule is bound to the tip of the oscillating CNT.
- The current flow through the CNT changes with diflection and thus the frequecy of the CNT oscillation can easily be determined by flowing current through the CNT and observing the frequency of the current ebb and flow through the CNT.
- This device was only simulated and would be quite tough to manufacture, and might not even be able to manufacture using bulk manufacturing processes, but suggested need for aligned patterened CNT cantilevers to detect different molecules by functionalizing a series of cantilevers caught my interest.

4.

Room Temperature sensor based on carbon nanotubes and nanofibres for methane detection

Roy, R., Chowdhury, M., & Pal, A.	2005	Vacuum
Chemical Sensing - CH_4	MWNT	semiconducting
Good Sensitivity	Unknown Selectivity	Reusuable with slight degradation over time, Probable Reproducibility
Response:	Market:	Mfg:

- For device fabrication thin film of MWCNT with diameters of 15-25nm and random direction was deposited on a SI wafer by electrolysis.
- CNT (sensitivity = [(Rair - Rgas) / Rair]) sensitivity was 70-80% in the presence of CH_4.
- Sensitivity was lowered over increased temperature as well as over repeated use.
- It was suggested that this methane sensor would be cheaper than other similar sensors and have the advantage of operating at room temp.

5.

Hydrogen sensors based on carbon nanotubes thin films

Sayago, I. et. al.	2005	Synthetic Metals
Chemical Sensing - H_2	SWNT	semiconducting
Good Sensitivity	Selective	Reusable and Reproducible
Response:	Market:	Mfg:

- A thin film of SWCNTs functionalized with palladium and depositied on an alumina substrate was used to make hydrogen sensors. This was done using palladium complex salts disolved in toluene.
- Unfortunately, the sensor had slow response and settling time (~30s) and the voltage change varied little over different concentrations of hydrogen (0.5%-4%)
- The sensors had sensitivity of 20% (sensitivity = 100 x [RH2- RN2] / RN2) which was hoped to be better. The sensors did at least detect H2 at room temperature where as plain SWCNTs and SWCNTs coated with palladium only operated at elevated temperature.

6.

Carbon nanotubes-based surface acoustic waves oscillating sensor for vapor detection

Penza, M. et. al.	2005	Thin Solid Films
Chemical Sensing - Alcohols	SWNT or MWNT	adsorption
Slightly Poor Sensitivity	Semi-Selective	Reusable, but Unknown Reproducibility
Response:	Market:	Mfg:

- CNT covered SAWs were used to make VOC sensors (in particular ethanol, ethylacetate, toulene sensors) that operate at room temperature. The SAWs were built, covered by SiO2, and then covered by SWNTs or MWNT mixed in ethanol or toulene.
- Full response took aprox. 20 min. which is not great but may be good enough.

7.

Kong, J. et. al.	2000	Science
Chemical Sensing	SWNT	semiconducting
Good Sensitivity	Semi-Selective	Reusable, but Unknown Reproducibility
Response:	Market:	Mfg:

- Single or conglomerate semiconducting SWNTs were used. Both NH3 and NO2 were detected with quick response time, two degrees of magnitude change in conductivity, repeatability over subsequent measurements.

8.

Carbon Nanotube Array-Based Biosensor

Sotiropoulou, S. et. al.	2002	Analytical Bioanalyitical Chemistry
Chemical Sensing -glucose	MWNT	functionalized
Good Sensitivity	Selective	Reusuable, but Unknown Reproducibility
Response:	Market:	Mfg:

- The sensors were made with aligned MWNTs were place on a platinum transducer, which were acid treated for 8h to remove amorphous carbon, tube caps, and shorten the tubes. The sensors were then functionalized by incubation for 3h in enzymatic solution of glucose oxidase.
- The sensors had sensitivity of 93.9 uA/ mM * cm2, with a linear response range from 0.25 mM to 2.5 mM and a minimum response of 0.19 mM.
- The sensors had sensitivity of 93.9 uA/ mM * cm2, with a linear response range from 0.25 mM to 2.5 mM and a minimum response of 0.19 mM.

9.

Single-walled carbon nanotube-based voltammetric sensor and biosensor

Xu, Z. et. al.	2004	Biosensors and Bioelectronics
pH Sensing	SWNT	electronic
Good Sensitivity	Selective	Reusuable & Reproducibility
Response:	Market:	Mfg:

- A thin film of SWCNTs on a glassy carbon electrode was found to have the voltage of peak current flow vary linearly with pH.
- The equation found for this pH dependence was Epa (V) 0.378 - 0.065 pH. It was found that this equation held fairly well over repeated measurements as well as over several electrodes.

10.

Carbon Nanotube Flow Sensors

Ghosh, S., Sood, A., & Kumar, N.	Feb. 2003	Science
Mechanical: Flow Sensing	SWNT	electronic: voltage generation
Great Sensitivity	Selectivity is NA	Reusuable & Reproducibility
Response:	Market:	Mfg: easy

- The device was manufactured by placing 0.2 mm thick mm film (length:1mm and width:2mm) is placed between electrodes.

- When liquid is flowed over the film a voltage is generated that increases with the log of the flow velocity, and also increases with the polarity or ionic charge of the liquid (i.e. HCl solution generates larger voltage at same flow rate as water.)
- The paper hypothesizes that this voltage generation is due to uneven charge distribution in the liquid instead of momentum transfer from the liquid to CNT phonons (due to the log dependence instead of linear dependence of voltage on flow rate.
- The 1 dimmensional attribute of CNTs seem important to flow sensing as MWNT are less sensitive and graphite has no sensitivity.
- Could have microfluidic application for array of sensors in pourous alumina.
- Maybe sort materials by polarities or electronegativity if flow through all channels are const?

11.

Preparation of Nucleic Acid Functionalized Carbon Nanotube Arrays

Nguyen, C. et. al.	2002	Nano Letters
Biological Sensing- DNA	MWNT (could use SWNT)	optical: tag flouresence
Good Sensitivity	Selectivity is NA	Reusuable? & Definitely Reproducible
Response:	Market:	Mfg:

- The device was created using aligned MWNTs supported with spin on glass (SOG) that were acid treated to remove the tips and the catalysts encapsulated in the tips.
- When spin on glass was not dispursed between the CNTs they tended to collapse during acid treatment
- The MWNT and SOG array was oxidized after the acid treatment to attach COOH groups to the CNT end. Then several solutions were added to attach nucleic Acids to the COOH groups, there by covalently binding the nucleic acids to the carbon nanotubes.
- The covalent binding worked well and was enhanced using an integrated siloxane film.
- Nucleic acid hybridization was also achieved.
- From figure the binding of nucleic acid to the CNTs didn't seem to be too even for what ever reason.

12.

Toward Large Arrays of Multiplex Functionalized Carbon Nanotube Sensors for Highly Sensitive and Selective Molecular Detection

Qi, P. et. al.	2003	Nano Letters
Chemical Sensing- NO_2 & NH_3	SC SWNT	semiconducting and functionalization
Amazing Sensitivity - 100 ppt NO_2	Semi-Selective	Reusable & Definitely Reproducible
Response:	Market: Gut feeling is fairly large	Mfg: Selective part difficult rest easy

- The array of sensors was manufactured by printing an array of pairs of moly electrodes

with the gap bet25ween the electrodes being fairly small.

- On either side of the gap between a pair of electrodes CNT catalyst was deposited on top of the moly and SWNT were grown by CVD to contact both electrodes across the gap.
- The formed sensors had 20-30 SCNTs attached to each pair of electrodes and due to the IV characteristic most of these SWNTs were semiconducting.
- It was found that immersing the sensors in a PEI/methanol solution doped the SWNTs n-type and made the sensor selective to electron accepting gases (i.e. detecting NO_2 but not NH_3, CO, CO_2, CH_4, H_2, O_2.) Similarly, Nafion made the sensors selective to NH_3 (picking up no signal from NO_2.)
- An array that detected NH3 and NO2 was created using microspotting to drop solution on each sensor individually allowing both Nafion and PEI covered sensors on the same array (very poor mass manufacturing process, but works.)
- The idea of detecting multiple gases with a single multiplexed array is quite interesting.

13.

A Wireless, Passive Carbon Nanotube-Based Gas Sensor

Ong, K., Zeng, K., & Grimes, C.	2002	IEEE Sensors Journal
Chemical Sensing- CO_2, O_2, NH_3	MWNT	capacitive
Poor Sensitivity - no better than 0.1%	Non-Selective	Reusable & Definitely Reproducible
Response: 45 s -CO_2, 20 min-O_2, 2 min - NH_3	Market: Gut feeling is fairly large	Mfg: Selective part difficult rest easy

- The device was created by creating a LC resonant circuit consisting of an interdigitated capacitor and square inductor. This resonator was covered with a SiO_2 layer followed by a coating of MWNT/SiO_2 composite layer.
- The adsorption of CO_2, O_2, NH_3 in the MWNT/SiO_2 layer changed the permitivity of the the layer affecting the capacitance of the capacitor and the resonant frequency of the LC circuit.
- This change in resonant frequency was measured remotely using a ring antenna.
- The change in dielectric permitivity is due to the electron doning or accepting of the gas when adsorbed on the CNT as well as the different permitivities of the adsorbed gas.
- The total change in permitivity is 4.4% when the gas is cycled from 80% N_2 and 20% O_2 to pure CO_2 (not very good.)

14.

Postgrowth Processing of Carbon Nanotube Arrays -- Enabling New Functionalites and Applications

Yin, A., Chik, H., & Xu, J.	Mar. 2004	IEEE Transactions on Nanotech.
	MWNT	

- This paper discusses the growth of large aligned arrays of CNT using an anodic aluminum oxide (AAO) template.
- The template was grown by a two step process at 40V resulting in a hexagonal structure and pores of aprox. 50 nm diameter.
- Cobalt was then deposited in the bottom of these pores and MWCNTs were grow at 600C using 10% acetylene supplied CVD.
- To etch the (AAO) a RIE surface clean was performed, followed by an etching in H3PO4/CrO3 and polymethacrylic acid (PMAA) or gum arabic (GA). The PMAA or GA was added to the acid to prevent the separated MWNT from bundling as the AAO is etched.
- This allowed separated arrays of 500-800nm long MWNT (diameter ~50nm) to be created using the AAO.

15.

Selective gas detection using a carbon nanotube sensor

Chopra, S. et. al.	Sept. 2003	Applied Physics Letters
Chemical Sensing - He, Ar, N_2, O_2, CO, NH_3	SWNT	capacitive
Poor Sensitivity	Non-Selective (in my opinion)	Reusuable & Reproducible
Response:	Market:	Mfg:

- The device was created by building a circular resonator and placing SWNT on the disk resonator.
- The carbon nanotubes were then placed in a chamber and degassed.
- The resonator was operated at 4GHz and the minimum shift occurred with He (0.8 MHz) and the maximum shift occured whit NH3 (3.5 MHz.)

16.

Multi-wall carbon nanotube as a new infrared detectied material

Liu, L. & Zhang, Y.	2004	Sensors and Actuators
Optical Sensing - IR	MWNT	semiconducting
Good Sensitivity	Semi-Selective	Likely Reusable, Reproducible Device (though not discussed)
Response:	Market: moderate	Mfg: could be easy

- The device was fabricated by depositing planar interdigitated copper electrodes on a Si substrate, then MWNT dispersed in chloroform were deposited on the electrodes using a langmuir trough method to obtain directional arrangement of the CNTs.
- Origionally, IR light shown on the CNTs did not induce a photocurrent but after a break down voltage of 40V was applied for aprox. 100s the device became sensitive IR light.
- This was explained as the voltage breaking down the metalic shells of the MWNT and leaving only semiconducting shells.

- The reason for the directional arrangements of the MWCNTs is to reduce or eliminate the problem of large dark current found in unordered MWCNTs.

17.

Characterization of E-glass-polypropylene interfaces using carbon nanotubes as strain sensors

Barber, A. et. al.	2004	Composites Science and Tech.
Mechanical Sensing - Strain	SWNT	optical - Ramen
Good Sensitivity		Non-Reusable, Not Reproducible b/c not really a device
Response:	Market: not really one	Mfg: custom to each interface

- The strain sensing was done by coating the surface of the E-Glass with a dispersed adhesive layer containing CNT followed by the CNT coated E-Glass being used in a polypropylene composite.
- Then using a laser to monitor the Raman spectrum of the CNTs the interface failure was determined and compared to a mechanical method of determining interface strength (the results compared well.)

18.

Near-Infrared optical sensors based on single-walled carbon nanotubes

Barone, P. et. al.	Dec. 2004	
Chemical Sensing	SWNT	optical flouresence quenching
Good Sensitivity - at least 1 mM glucose	Selective	Reusable, Reproducible Device
Response: 80s	Market: depends on enzyme detection	Mfg: seems fairly easy

- The device was by suspending semiconducting SWNT in a buffered solution and coating them with a monolayer of glucose oxidase (or some other protein or enzyme.)
- When certain molecules bind to the glucose oxidase the emission spectrum (due to IR excitation) of the CNTs can be quenched.
- A device, that was suggested could be placed under the skin of a diabetic to continuously monitor glucose levels, was made out of the dispersed covered SWNT in a mircocuvette with a membrane to keep the CNTs in but allow the exchange of glucose over the membrane.
- A light emitter and detector could then be shined through the skin to continuously monitor glucose levels.

19.

Diamond and carbon nanotube glucose sensors based on electropolymerization

Loh, K., Zhao, S., & Zhang, W.	2004	Diamond and Related Materials

Chemical Sensing - glucose	MWNT or SWNT	functionalization
Good Sensitivity - less than 1 mM	Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

- The device was fabricated by using cyclic voltmetry to attach 3,3 diaminobenzideine (DAB, a non-conducting polymer) to a CNT carpet on a platinum electrode.
- Cyclic voltmetry was then used to attach Glucose Oxidase to the polymer coated CNTs.
- This device had a good linear amperometric response to added glucose and was selectively detected glucose while not generating a response to ascorbic acid and uric acid (typical interferent molecules.)
- The DAB also seemed to lower the necessary amperometric bias to detect glucose to 0.3V from 0.5V for glucose oxidase covered CNTs. The higher bias for CNT without DAB caused the interferent molecules to generate a small signal.

20.

Direct Generation of a Voltage and Current by Gas Flow Over Carbon Nanotubes and Semiconductors

Sood, A. & Ghosh, S.	Aug. 2004	Physical Review Letters
Flow Sensing - Gas	SWNT & MWNT	temp. differential
Good Sensitivity		Reusable, Reproducible Device
Response:	Market:	Mfg:

- The the device is a simple layer of SWNT or MWNT (or any other material for that matter) attached at either end to electrodes.
- The flow of gas over this substrate held at 45 degrees to the chamber surface generates a voltage across the material.
- This voltage is due to a pressure differential created across the material, which generates a temperature differential and by the Seebeck effect generates a voltage that depends on the square of the flow velocity.

21.

Carboxylation multi-walled carbon nanotubes modified with $LiClO_4$ for water vapour detection

Huang, X. et. al.	2004	Nanotechnology
Chemical Sensing - water vapor	MWNT	semiconducting
Good Sensitivity - ppm	Semi-Selective	Reusability & Reproducibility not discussed
Response: on- 8 min, off - <1 min	Market: reasonable	Mfg: lots of steps

- The paper was far from being the best I've read. It had many typos and seemed to lack a bit of coherent explaination at points.
- The two interesting parts was the large change in resistance of the $LiClO_4$ covered

nanotubes when water vapor was introduced, the 5 orders of magnitude seemed the larger than what I can remember of resistance change in plain MWNT (I could be wrong of course.)

- Second they describe a dynamic response of the CNTs that seems to give a way of at least selectively telling the difference between the presence of plain air and the presence of water vapor.
- The preparation of the $LiClO_4$ covered nanotubes due to the growth of MWNT with poor purity took a large number of steps in this paper.

22.

Recovered Bandgap Absorption of Single-Walled Carbon Nanotubes in Acetone and Alcohols

Cao, A. et. al.	2005	Advanced Materials
Chemical Sensing- CH_4 & acetone	SWNT	optical
OK Sensitivity	Possibly Selective	Reusable, Reproducible Device
Response: not mentioned	Market:	Mfg:

- A SWNT film was created by depositing arc discharge created CNT dispersed in acetone on a quartz substrate.
- The film was then exposed to slightly humid air for 2 days, and then the optical absorption spectrum of the CNT was taken.
- It was found that after dropping acetone on the air exposed CNT the ratio of S1/S2 (the two CNT absorption peaks) recovers rapidly and linearly up to 0.3 mL of acetone dropped, followed by recovery that plateaus at 3 mL.
- It is beleived that the recover of the S1 peak is due to H_2O being cleaned or deadsorbed from the CNTs by acetone. This is supported by the fact that preheated CNT have a larger S1/S2 ratio then air exposed CNT and acetone does not increase the S1/S2 ration anymore or increase the absorption spectrum anymore.
- It was found that methane recovers the absorption spectrum the best while liquids that are not soluble to water do not recover the absorption spectrum.
- It is suggested that if different solvents have separate affinities to different adsorbate this could lead to the selective detection of different molecules.

23.

Nanotube Molecular Wires as Chemical Sensors

Kong, J. et. al.	2000	Science
Chemical Sensing - NO_2 and NH_3	SWNT	semiconducting
High Sensitivity - ppm	Semi-Selective	Reusable, Reproducible Device
Response: 10 s, 1 h recovery	Market: fairly large	Mfg:

- Interesting paper on the first tests of SWNT used for gas detection based on semiconducting resistance change with the adsorption of gas.
- Mentions that biasing the SWNT with different voltages can lead to some additional

selectivity.

- Metallic SWNT were also found to change resistivity when exposed to different gasses, however their conductivity change much less due to the adsorbed gas molecules.
- The paper compared the operation of S-SWNT for NO_2 sensing at 200 ppm to that of currently available conventional NO_2 sensors.
- The SWNT sensors had a 10 time faster response and 2 to 3 time greater sensitivity and could operate at room temperature, compared to a metal oxide sensor (the best of the mentioned sensors) that operates at 250 C, however the SWNT sensor had a 10 to 100 time slower recovery to its original resistivity.

24.

1/f noise in single-walled carbon nanotube devices

Snow, E. et. al.	Sept. 2004	Applied Physics Letters
	SWNT	
Response:	Market:	Mfg:

- Discusses the noise characteristics of carbon nanotube devices, which is important to any device with electrical transduction.

25.

Low-resistance gas sensors fabricated from multiwalled carbon nanotubes coated with a thin tin oxide layer

Liang, Y. et. al.	July 2004	Applied Physic Letters
Chemical Sensing - NO & NO_2	MWNT	adsorption
Good Sensitivity - ppm	Semi-Selective	Reusable, Reproducible Device
Response: 10s	Market: reasonable	Mfg: fairly easy

- The device was manufactured by coating MWNT on a ceramic tube, covering the MWNT with SnO_2 and attaching Pt electrodes to either end of the tube. In order to heat the sensor a resistance heater was placed inside the ceramic tube.
- The device showed reasonable sensitivity to NO, NO_2 and Ethanol.

26.

Influence of molecular adsorption on the dielectric properties of a single wall nanotube: A model sensor

Langlet, R. et. al.	Nov. 2004	Journal of Chemical Physics
Chemical Sensing - NO_2, H_2O, etc.	SWNT	capacitive
Low Sensitivity	Semi-Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

- The interesting part of this paper compared with other papers i that it found that hexane and C_3H_7Br prdouce reasonable large changes in dielectric permitivity which would allow for some what reasonable sensitivities towards them.

27.

Chemically Functionalized Single-Walled Carbon Nanotubes as Ammonia Sensors

Bekyarova, E. et. al.	2004	Journal of Physical Chemistry
Chemical Sensing - NH_3	SWNT	functionalized
High Sensitivity - ppm	Selective	Reusable, Reproducible Device
Response: 1 min, ~10 min recovery	Market: unknown	Mfg: fairly easy

- The SWNT were deposited on interdigitated gold electrodes and then functionalized with poly-(m-aminobenzene sulfonic acid) (PABS.)
- It was found that the PABS increased the sensitivity of the device and increased the signal change two fold while decreasing the response time.
- The PABS also seemed to decrease the amount of NH_3 that chemisorbed which could increase a devices perfomance over time.

28.

Electronic Properties of Carbon Nanotubes with Covalent Sidewall Functionalization

Zhao, J. et. al.	2004 SWNT	Jounal of Physical Chemistry
Response:	Market:	Mfg:

- The paper discusses some interesting effects of sidwall attachment of functional groups to SWNT.
- It discusses the effects of sidewall chemical functionalization based on COOH bonding and physical boding of functional groups.

29.

Dielectrophoretic Batch Fabrication of Bundled Carbon Nanotube Thermal Sensors

Fung, C. et. al.	Sept. 2004	IEEE Transactions on Nanotech.
Thermal Sensing	MWNT	
		Reusable, Reproducible Device
Response:	Market: probably low	Mfg:

- This paper discusses the batch fabrication of devices made by aelectrophoretic technique that allows the placement of CNT bundles across microfabricated electrodes.
- They claim that this technique would allow for inexpensive thermal sensors, but the main selling point would definitely have to be that thermal devices smaller then are possible now could be made.

30.

Effects of Oxygen annealing on cross sensitivity of crabon nanotubes thin films for gas sensing applications

Valentini, L. et. al.	2004	Sensors and Actuators
Chemical Sensing - NO_2	SWNT	semiconducting
High Sensitivity - ppb	Semi-Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

- This paper shows that semiconducting nanotubes can be converted into metal CNTs through oxidizing procedures.
- This can also change the selectivity of the SWNT to NH_3 and H_20.

31.

A simple approach in fabricating chemical sensor using laterally grown multi-walled carbon nanotubes

Jang, Y. et. al.	2005	Sensors and Actuators
Chemical Sensing - NH_3	MWNT	semiconducting
Good Sensitivity	Semi-Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

- This paper discusses the lateral growth of MWNT between predefined Nb electrodes.
- This method is expected to yield easily manufacturable devices.
- The NH3 testing of the device probed the device to operate as well as other similar devices.

32.

Interaction of methane with carbon nanotube thin films: role of defects and oxygen adsorption

Valentini, L. et. al.	2004	Material Science & Engineering
Chemical Sensing - O_2	SWNT	adsorption
	Semi-Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

- The paper suggest that the sensitivity of CNT to methane may be due to O2 contamination.
- This is interesting as several papers discuss methane detection of CNT and this calls their

results into question.

33.

Ab Initio Study of Doped Carbon Nanotube Sensors

Peng, S. & Cho, K.	Feb. 2003	Nano Letters
Chemical Sensing - NO_2, NH_3, O_2	SWNT	semiconducting
High Sensitivity - ppb	Semi-Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

- This paper discusses the substitutional doping of SWNT with boron and nitrogen creating composite nanotubes.
- These devices were found to have variable sensitivity to the presence of CO and H_2O based on the doping levels of the CNT.

34.

Photoconductivity in Semiconducting Single-Walled Carbon Nanotubes

Akihiko, F. et. al.	2001	Jap. Journal of App. Physics
Optical Sensing	SWNT	semiconducting
Average Sensitivity - 100 nJ pulse	Semi-Selective	Reusable, Unknown Reproducibility
Response:	Market:	Mfg:

- While not specifically mentioned, the graphs of IR illumination may suggest evidence that dark current limits photocurrent measurements below 0.1 uA (in response to claim by Liu, L in (16))
- Uses SWNT making Liu, L use of MWNT in (16) the only paper to suggest quantum IR detection in MWNT due to photocurrent, limits evidence for hypothesis that allignment of MWNT is what reduces dark current.
- Two peaks in photocurrent were detected at 0.7 eV and 1.2 eV which are close first and second interband gap of S-SWNT with diameter of 1.4 nm according to authors.
- The peaks match up with adsorption spectrum as well.
- No photocurrent seems to be generated by incident light with photons of energy less than 0.5 eV.
- The photocurrent of the first peak at 0.7 eV is much larger at 13.2 K versus room temp. while the second peak at 1.2 eV is less affected.
- The authors try to explain the difference in peaks based on charge transmission in CNT, but at least the attempted explainations fail.

35.

Multi-walled carbon nanotubes experiencing electrical breakdown as gas sensors

Chung, J. et. al.	2004	Nanotechnology
Gas Sensing - O_2	MWNT	shell adsorption?
Average Sensitivity	Unknown Selective	Reusable, Reproducible Device

Response: Market: Mfg:

- This paper cites research that suggest that O_2 adsorption on SWNT surface has less effect on charge transport than usually believed, instead to account for increased conductivity of CNT when exposed to air, in comparison to vacuum, it is suggested that O_2 adsorption to defect sites or at the CNT-electrode junction is responsible for the increase.
- This paper places a single MWNT across an electrode using a CEGA technique.
- The resistance of ~22 nm diameter arc-discharge CNTs were ~100 KOhm, while mainly ~100 nm diameter CVD grown MWNT were ~10 KOhm (suggested that this is due to larger diameter, does this mean all shells conduct?)
- The threshold for electrical breakdown of large diameter MWNT is ~1 V and for small diameter MWNT ~3 V.
- Break down of inner shells often occurred before entire outer shell was removed.
- Break down often occurred around defects and was sometime localized btw. defects.
- Small diameter MWNT (both arc-discharge and CVD) didn't have increased charge transport due to O_2 partial pressure changes, but large diameter MWNT did have increased charge transport.
- It is suggested that this supports the idea of O2 affecting charge transport by reducing CNT-electrode Schottky barrier or facilitating charge transport from broken outer shells to inner shells, they focus on the possible mechanism of transport btw. shells.
- The breakdown voltage of the MWNT might call into question the results of the IR sensor by Liu (16), unless multiple MWNT would require higher break down voltage, than a single MWNT.

36.

Escherichia coli single-strand binding protein-DNA interactions on carbon nanotube-modified electrodes from a label-free electrochemical hybridization sensor

Kerman, K. et. al.	2005	Anal. Bioanal. Chemistry
Biological Sensing-DNA & Protein	SWNT	Cyclic Voltametry
Sensitivity - 1 ug/mL	Selective	Non Reusable, Reproducible Device (life time 1-1month)
Response: 20 min	Market: good	Mfg:not too hard

- The paper described the use of CNT to detect the presence of DNA hybridization by binding protein to unhybridized single strand DNA probes and thus change the peaks observed by cyclic voltametry.
- E coli single-strand binding protein binds selectively to single strand DNA and not double strand DNA, when it is bound it also reduces the normal guanine voltametry peak seen in the presence of DNA and introduces a Tyrosine and Tryptophan redox peak.
- This paper seems to contain very well done research though the uses of tons of unfamiliar terminology makes it a difficult read.

37.

Sonication-induced changes in chiral distribution: A complication in the use of single-walled carbon nanotube fluorescence for determining species distribution

Heller, D. et. al.	2005	Carbon
	SWNT	
Response:	Market:	Mfg:

- Sonication dispersed CNT display different spectrofluoresence depending on the type of sonication used.
- This is because sonication tends to cleave CNT to different sizes, randomly changing the lengths of CNT and causing the chiral distribution determined by spectrofluoresence to change.

38.

Piezoresistance of carbon nanotbues on deformable thin-film membranes

Grow, R. et. al.	2005	Applied Physics Letters
Mechanical Sensing - pressure	SWNT & MWNT	curvature bandgap changes
Average Sensitivity - 1 psi		Reusable, Unknown Reproducibility
		Device
Response:	Market:	Mfg:

- This paper described the electromechanical response of CNT on a SiN membrane by inducing strain in the CNT with pressure deflection of the membrane (similar to a pressure sensor.)
- The CNT were contacted at each end with Pd electrodes and a common gate electrode was placed on the opposite side of the SiN membrane; this allowed I_{ds}-V_g measurements with changing pressures and therefore strains.
- It was found that the CNT (all of which exhibited SC char.) when in the FET off regime had quite reasonable changes in conductivity (both increasing and decreasing depending on the CNT).
- In calculating the bandgap of the CNT and the change of the band gap with strain there were several descrepancies found.
- The small gap tubes (SGS) which had n-m = 3q and therefore a gap only dependent on curvature had band gaps of greater than the predicted maximum of 20 meV, they exhibited both positive and negative conductivity changes when only negative changes in conductivity were expected due to strain, and both SGS and semiconducting CNT had changes in band gap due to strain that exceded the maximum expected strain.
- It was suggested that all the above phenonomenon might be explained by CNT-SiN suface interactions and the rough SiN surface, that could cause collapse and torsion of the CNT and that some of the SGS CNT might have been metallic with surface induced band-gaps.
- This paper basically mentions that surface and inter-tube interactions can greatly affect band-gaps.

39.

Photoconductivity of single-wall carbon nanotubes under continuous-wave near-infrared illumination

Levitsky, I. et. al.	2003	Applied Physics Letters
Optical Sensing - IR	SWNT	semiconducting adsorption
OK Sensitivity - 50 mW/mm		Reusable, Reproducible Device
Response: slow, several s	Market:	Mfg:

- This paper studied steady photocurrent induced by light in films of SWNT placed across electrodes of various gap sizes.
- The SWNT were grown by a arc discharge and had diameters of 0.8-1.1 nm.
- The induced photocurrent had a linear response to light intensity, but had dark current drift and a slow rise/decay (4-5 s relaxation time)
- The explaination of dark current drift due to adsorbed O_2 seemed to be backed up if a bit odd, but the explaination of the slow responses due to O_2 trapping was hard to understand and odd as well.
- This paper also claims reduced electron-phonon coupling in nanotubes, and that this causes reduced dark current in CNT, yet they seem to have a decent amount of dark current in this experiment, and do not cite research to back up reduced electron-phonon coupling.

40.

Chemical Detection with a Single-Walled Carbon Nanotube Capacitor

Snow, W. et. al.	2005	Science
Chemical Sensing - many gases	SWNT	capacitive
High Sensitivity - as low as 0.5 ppb	Semi-Selective	Reusable, Reproducible Device
Response: sometimes faster than 4s	Market:	Mfg:

- This paper describes the simple creation of a CNT capacitor with chemoselective polymer layer that can selectively detect many groups of gases with high sensitivity and fast response.
- There seems to be a trend of increasing sensitivity with increasing dipole moment.
- It is suggested that many (or all) of the exceptions to the above trend happen to polarize parallel to the SWNT surface and that perpendicular polarization is necessary for dielectric change.
- Finally they expect that the capacitance response should scale as Pu^2, P = pressure, and u = dipole moment, and notice that there are large deviations from this.
- This suggests to me (especially from my observations in other papers cover CNT capacitive sensors that didn't use the CNT as electrodes) that the capacitance depends more on the molecular polarizability than the dipole moment and thus would suggest a linear scaling of the capacitance response.
- It is possible that aligned CNT would increase the capacitance response by aligning the polarized gas molecules but seems a bit unlikely.

41.

Multiple Enzyme Layers on Carbon Nanotubes for Electrochemical Detection Down to 80 DNA copies

Munge, B. et. al.	2005	Analytical Chemistry
Biological Sensing - DNA	SWNT	electrochemical
High Sensitivity - 80 DNA copies	Selective	Reproducible Device (reusable using different methods to reverse hybrid.)
Response:	Market:	Mfg:

- Discusses a method to maximize CNT tag coverage.
- This allows the best known DNA amplification to date.

42.

Application of carbon nanotubes for detecting anti-hemagglutinins based on antigen-antibody interaction

Takeda, S. et. al.	2004	Biosensors and Bioelectronics
Biological Sensing - viruses etc.	SWNT	electrochemical
Good Sensitivity	Selective	Reproducible Device
Response:	Market:	Mfg:

- Discusses the use of CNT on glassy carbon electrodes to detect flu virus membrane proteins and could be applied to the detection of other complex proteins.

43.

Coiled Carbon Nanotubes as Self-Sensing Mechanical Resonators

Volodin, A. et. al.	2004	Nano Letters
Mechanical Sensing - accoustic vib.	MWNT	resonance freq. change
Good Sensitivity - 100-400 MHz		Reusable, Reproducible Device
Response:	Market:	Mfg:

- This paper manufactured a mechanical resonator by depositing coiled CNT (created by catalytic decompositiontion of acetylene) on gold electrodes.
- Upon accoustic vibration of these coils they generate a change in the resistance of the CNT allows the frequency of the vibration to be measured.

44.

Computational design of carbon nanotube electromechanical pressure sensors

Wu, J. et. al.	2004	Physical Review
Mechanical Sensing - pressure	SWNT	bandgap bending

High Sensitivity - ppb	Semi-Selective	Reusable, Reproducible Device
Response:	Market:	Mfg:

- This paper discusses the conceptual design of a CNT pressure sensor.
- The paper uses an array of SWNT with varying diameter and armchair chirality to sense a large spectrum of pressures.
- This would allow MEMS pressure sensors of much better sensitivity and more measurement breadth than currently available, however would this be worth the extra cost? I don't know.
- This sensor is probably best used in a conjuction with other parts to create a larger MEM system.

45.

Laser applications heat up for carbon nanotubes

	2005	nanotechwire.com
Optical Sensing	MWNT	thermal
		Reusable, Reproducible Device
Response:	Market:	Mfg:

- This article discusses the use of a CNT film for its thermal conductivity to create an improved IR thermopile.
- This thermopile would allow for improved laser characterization.
- Unlikely to catch on until CNT cost come down a ton due to current thermopiles being extremely cheap, and don't know if the extra sensitivity and response time would be valued enough to pay for the extra cost of CNTs.