

Carbon Nanotube based Microwave Resonator Gas Sensors

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This paper reviews our work on the development of microwave carbon nanotube resonator sensors for gas sensing applications at the University of California at Davis. The carbon nanotube sensor is a passive circuit that does not rely on battery for operation. Our experimental results demonstrate that the microwave carbon nanotube resonator sensor achieve a sensitivity of 4000 ppm/Hz. This sensor platform has great potential for wireless sensing network applications.

Keywords: carbon nanotubes, wireless, sensor, and remote.

I. Introduction to Carbon Nanotube Gas Sensors

Chemical sensors are currently one of the most important research areas. The ability to monitor our environment is becoming increasingly important. With the world market for sensor microsystems estimated to be greater than \$38 billion¹, the current demand is already extraordinary with many applications yet to be realized. From improving the efficiencies of industrial processes, to monitoring changes in our planets ecosystem, and to ensure national security the possibilities for reliable, sensitive, compact, and cost efficient sensors are overwhelming. Despite many difficulties, the recent successes in the field carbon nanotube chemical and biological sensors offer excellent promise in the near future.

Gas sensors have various implementations. The most common implementation to date is the semiconductor sensor. Semiconductor sensors use the charge transfer from/to an impurity to/from the transducing material (the semiconductor). This causes a change in the carrier concentration which manifests itself as a resistance change in the material. Metal oxides are the most commonly used material with the main disadvantage being that they require relatively high temperatures ($\sim 200\text{ C}^0$)²⁻¹⁰. Another technique receiving a fair amount

of attention in recent years is the SAW sensors. Although implemented on a platform suited for wireless applications, demonstrations of its utility as a gas sensor have not been compelling due to low sensitivity¹¹⁻²³. Other techniques used for gas sensing include optical fibers terminated or coated with a sensing material, infra-red spectroscopy, and various mass spectroscopy techniques currently used in laboratories. Although these methods are very precise, their size and cost prohibit them from wide acceptance²⁴⁻²⁸. Another technique similar to semiconductor sensors is the use of nano-structured sensors. Most of the nano-structured materials used are also semiconductors. Currently, three of the most popular materials are nanobelts¹⁰ (suffering from the same temperature restrictions as metal oxides), nanowires, and carbon nanotubes, the subject of this paper.

Nanotechnology can offer solutions to scalability, integration, and sensitivity issues that have plagued traditional technologies- a fact that was already recognized by Gopel in 1991²⁹. In nanomaterial based sensors, sensitivity increases of six to eighteen orders of magnitudes are theoretically and practically possible: The detection of single molecules by Cu nanowire based sensors has already been reported³⁰. Sensing will also become much faster. By introducing transducers with nanoscale dimensions, the lengths of electrical connections are decreased, and sensing speeds can be increased substantially. Nanoscale phenomena such as conductance quantization³¹ and single electron charging³² will be utilized for sensing purposes. The required techniques (scanning tunneling microscopy (STM), atomic force microscopy (AFM), near-field scanning optical microscopy and laser spectroscopy) for the detection of these novel phenomena are already available.

Particular interest exists in using nanowires of semiconducting and metallic^{33, 34} materials as sensor elements. The advantage of these one-dimensional electrical conductors is that they can be employed for both detection and signal transduction. Chemically modified and non-modified nanowires for biochemical and gas sensor applications were fabricated by Yang³⁵ and Lieber³⁶.

Similar applications have been realized with carbon nanotubes. As shown by Dai and coworkers,³⁷ gases such as NO₂ can change the electrical conductivity of carbon nanotubes by three orders of magnitude even at a concentration of only 20 ppm. Collins³⁸ obtained similar results when exposing carbon nanotubes to oxygen. These reported sensitivities, as well as very short response times, substantially exceeded the performance of comparable solid-state sensors.

Nano-structured materials have been used as the sensing material in three main categories of sensors: the SAW sensor^{11, 15-22}, conductivity sensors, and spectral domain

sensors. SAW sensors, as mentioned above, suffer from the drawback of low sensitivity. Conductivity sensors, on the other hand, have relatively high sensitivity and have been used with a wide range of materials^{2-10, 36-52}. Conductivity sensors operate at DC and have two common implementations. The first is simply using the sensing material as a resistor, and the second involves using the material as the channel of a FET. Upon exposure to impurities, the material will change its conductivity, which will be sensed as either a current or voltage change. Conductivity sensors have been used with a wide range of materials. Metal oxides have had much success in gas sensing²⁻¹⁰, but due to the temperature requirement, they are not suited for wireless applications. Conductive polymers^{43, 52-53} and carbon nanotubes^{37-41, 44-51} have been demonstrated to operate at room temperature, and the use of mass selective polymer coatings⁵³ offers potential of improving the sensitivity of Nanotube based sensors. The essential drawback with these sensors is their response time, which improves with temperature⁵⁴.

Spectral domain sensors⁵⁵⁻⁶⁵ are very similar to conductivity sensors, except that changes in conductivity at a frequency or over a range of frequencies are used to determine the concentration of impurities. These structures can simply be conductivity devices operated at higher frequencies, where the concentration of the impurities would be deduced from the change in transfer characteristics of the material⁶². They can also be capacitors, planar inductors⁵⁶, microwave resonators^{39-40, 58-62}, or simply a terminated transmission line⁵⁵. The choice of where to put the sensing material on these structures depends on where it will have the greatest effect on performance when its properties change as well as where it will be the most exposed to the environment. These sensors have been constructed with the materials mentioned above, with the same limitations. Spectral domain sensors offer one significant advantage over conductivity sensors in that they can operate at a frequency suited for wireless transmission. Thus, impedance sensors are capable of creating wireless sensor nodes with minimal complexity, as shown by Yoon⁵⁵ and Kong⁵⁶.

The remainder of this paper consists of six sections. First we will present a brief review of sensor terminology. Second, we will discuss the electrical properties of carbon nanotubes, as well as a brief explanation of the sensing mechanism. Third, we will describe the work we have done at U.C. Davis, providing a summary of our design process, experimental setup, experimental results, and further discussion regarding the sensing mechanism. The remaining sections will review recent developments in wireless gas sensing nodes, functionalizing carbon nanotubes for specific applications, and, finally, describe our future research in the development of the microwave carbon nanotube resonator sensors here

at the University of California at Davis.

II. Review of Gas Sensor Terminology

Gas sensors must meet a variety of criteria in order to be practical. The sensor must respond within a relatively short time period to give an accurate assessment of the current impurity concentration. Response time is usually used to specify the time interval required for the sensor to stabilize at its final value. Other terms are sometimes used to characterize the response time such as rise time. This term is used to characterize the time required for the sensor response to reach a certain percentage of its final value.

Sensors should also be reusable for wide acceptance. The characterization of how long the sensor takes to return to its initial state is its recovery time. Recovery time generally refers to the amount of time required for the sensor to stabilize at its initial state. Fall time (or rise time depending on the sensor's response) may also be used and refers to the time interval required for the sensor to return to some percentage, usually ninety, of its initial state. Recovery is one of the main obstacles of carbon nanotube based sensors, which can take several hours.

Sensitivity is used to characterize the change in the sensor's response for a given concentration of gas. Obviously, the amount of change for a given concentration of gas is of primary importance. In this paper sensitivity will refer to the sensor response, characterized by frequency shift, divided by the concentration in ppm. The linear range of the sensor response corresponds to the range of concentrations for which the sensitivity is constant. Linearity in the response is desirable. However, as long as the response is monotonic, and repeatable, this is not a major concern.

Another important parameter is selectivity. It is highly desirable that the sensor respond to a narrow range of gases to avoid the situation of false interpretations of readings. Purified as-prepared nanotubes interact with oxidizing/reducing species, with oxygenation at defect sites accounting for most of the observed results. While it is possible to greatly reduce and perhaps eliminate the response of the sensor to oxygen, the sensor will respond to any oxidizing/reducing species in its environment. Also, there are many species that are of a concern for health or industrial applications that do not cause an appreciable response in the nanotubes. Many efforts are currently underway to functionalize the nanotubes to tailor the selectivity for a particular application. Palladium⁶⁶ and the construction of CN_x ⁶⁷ tubes have been suggested to address this problem.

III. Properties of Carbon Nanotubes and Mechanisms for Gas Sensing

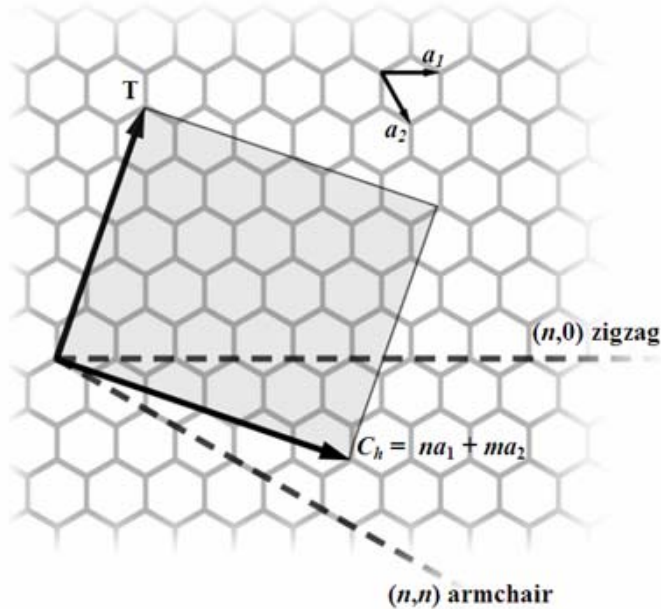


Figure 1. Illustration of the chiral vector (C_h) in terms of vectors a_1 and a_2 ⁶⁸

Carbon nanotubes possess very high aspect ratios and are essentially all surface area. The two main aspects of the nanotube that determine its electrical properties are its diameter and chirality. If the nanotube is envisioned as rolled graphite sheet, the tube's chirality is determined by how the sheet attaches to itself. The chiral vector is defined as $C_k = n \times a_1 + m \times a_2$ (note the vectors a_1 and a_2 are not orthogonal, see Fig. 1). Imagining the nanotube being unrolled into graphite sheet, the chiral vector is between two equivalent sites representing where the graphite sheet attaches to itself to form the nanotube. The vector is directed along the circumference of the tube and normal to its axis. The magnitude of the vector is equal to the diameter of the tube, while its direction indicates its chirality. Carbon nanotubes have three distinct categories classifying their chirality: armchair, zig-zag, and chiral tubes. Zig-zag and armchair tubes are referred to as achiral tubes, while all other tubes are chiral tubes. Tubes are also classified as being either metallic or semi-conducting. All armchair tubes, described by $n=m$, are metallic. Zig-zag tubes, described by $m=0$, are metallic if n is a multiple of three. The condition in its most general form can be stated as the difference between n and m must be a multiple of three. The conditions for the nanotubes to be

metallic are equivalent to the chiral vector intersecting the points where valence and conduction bands in the Brillouin zone of the equivalent graphite sheet are degenerate, and, therefore, no band gap occurs. For the tubes having a band gap, the band gap is inversely proportional to the diameter of the tube⁶⁹.

Nanotube sensors rely on the transfer of charge from the species to be detected to the nanotubes. Conductivity sensors measure this directly in that the charge transfer either increases or decreases the number of free carriers^{38, 41, 44-51}. The change depends on the state of the tubes and the direction of charge transfer. Most nanotubes are p-type due to oxygenation at defect sites^{38, 41}. Therefore, oxidizing species accept electrons, increase the number of holes, and thus increase the conductivity. Reducing species donate electrons to the tubes, tend to fill the holes, and reduce the conductivity⁷¹. Spectral domain sensors, the subject of this paper, involve monitoring the impedance of the sensing structure. In the sensor presented here, impedance is monitored by observing the magnitude of S_{11} of a microstrip resonator, coated with carbon nanotubes, and the frequency of resonance, determined by the nanotube coating, indicates a relative concentration of impurities. The frequency of resonance can be determined by the sharp dip in the S_{11} , indicating that energy is transmitted to the resonator with little or no reflection. The change in resonant frequency is most easily understood by considering the complex permittivity. The imaginary part of the permittivity, representing loss, increases with conductivity. The real part increases with conductivity due to the screening effect of the mobile charges. Permittivity indicates how an electric field will behave in a material. By changing this behavior in the nanotube cover, impurities alter the resonance condition of the resonator and cause a change in the resonant frequency. An increase in the real part of the permittivity of the nanotube cover will decrease the resonant frequency and vice-versa. Other conductivity sensors use the same effect, in different ways. In the work of Yoon et al⁵⁵, the phase of S_{11} of a carbon nanotube terminated coplanar waveguide is used for detection. In Kong et al⁵⁶, the impedance of a planar tank circuit, coated with carbon nanotubes, is monitored around 10MHz.

IV. Wireless Carbon Nanotube Gas Sensor

4.1 Sensor Design

The microwave circular disk resonator was designed on a Duroid board (RO4350B) that has a dielectric constant of 3.48 and a thickness of ~ 1.5 mm. The resonant frequency was first determined by an approximate formula for the resonant frequency at the dominant mode:

$$f_0 = \frac{1.841c}{2\pi a\sqrt{\epsilon_r}}$$

where f_0 is the resonant frequency of the resonator, c is the speed of light in vacuum, a is the radius of the disk, ϵ_r is the relative dielectric constant of the substrate (Duroid board). The resonator can be scaled to higher frequency to achieve greater sensitivity and reduce device size. Capacitive gap was designed to couple RF electromagnetic energy in and out of the circular disk resonator. A $50\text{-}\Omega$ transmission line was used to feed RF signals into the resonator with a gap of $\sim 200\mu\text{m}$. The dimensions of the gap were designed so that the return loss at resonant frequency is beyond 20 dB. The Sonnet[®] electromagnetic tool was used to optimize the capacitive gap for optimum impedance at the resonant frequency. A 3.5 mm connector was soldered to the other end of the microstrip line to provide connection to a microwave vector network analyzer.

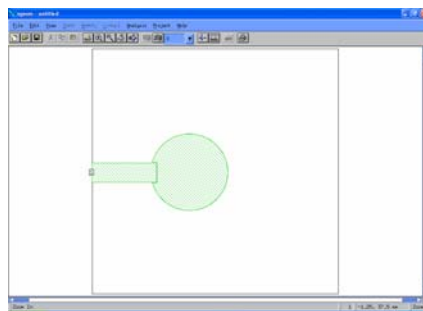


Figure 2. Model used in Sonnet[®] simulation

Single wall carbon nanotubes (SWNTs) and multi-wall carbon nanotubes (MWNTs) can be assembled on top of the resonator disk to form a transducer for gas sensing. The microwave carbon nanotube resonator sensor is configured in a 1-port device of which the

frequency response return loss or reflection coefficient will be used to determine the resonant frequency. Figure 3 shows a diagram of the microwave carbon nanotube resonator sensor and its cross section.. In our current design, we employ single wall carbon nanotube powder purchased from Carbon Nanotechnologies Incorporated⁷⁰. The single wall carbon nanotubes have diameters ranging from .8 to 1.2 nm with the average being 1nm. The lengths of the nanotubes range from .8nm to 10000 nm. The single wall carbon nanotube powder is purified to 14% Fe by weight. The carbon itself is 95% nanotubes and the rest consist of amorphous carbon and partial fullerene structures. The nanotubes are roughly a third conducting, a third semi conducting, and a third insulating. The carbon nanotubes were applied to the copper disk by applying a thin layer of conductive epoxy and pressing the nanotube powder on top of the epoxy. The result is a dense, thin layer of randomly orientated tubes with a high number of defect sites due to pressing the nanotubes. The thickness of the carbon nanotube is $\sim 5 - 10 \mu\text{m}$. The application of carbon nanotubes and conductive epoxy to the surface of the resonator causes degradation in the performance of the resonator which necessitates manual tuning of the structure afterwards. Figure 4 shows a picture of an actual prototype.

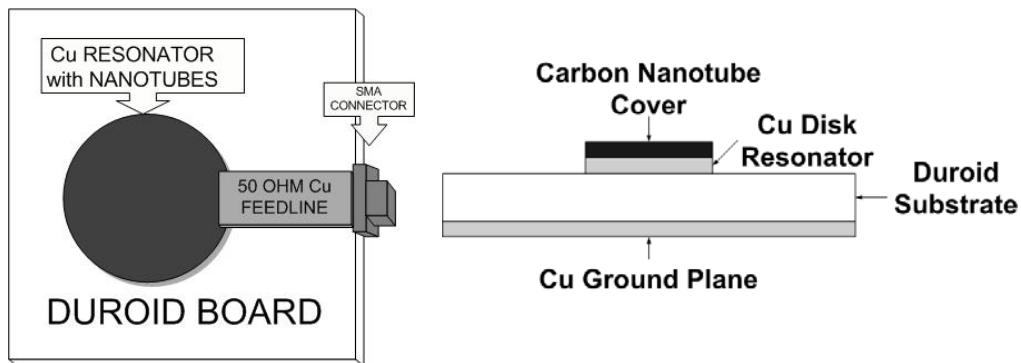


Figure 3. Diagram of Microwave Carbon Nanotube Resonator Sensor and its cross section..

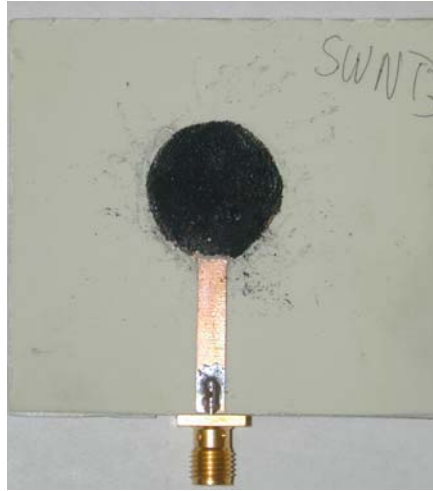


Figure 4. Picture of a prototype

4.2 Experimental Set-Up

Figure 5 shows the testing set-up for measuring the microwave carbon nanotube resonator sensor. The testing chamber has an RF feed-through coax cable to provide high frequency testing signals to the sensor. The sensor prototype is placed inside the testing chamber and is monitored using an 8364B Agilent Performance Network Analyzer (PNA). Due to the degradation in the performance of the resonator from the application of the carbon nanotubes, an impedance tuner was used to match the resonator and coax feed line to 50 Ohms at the resonant frequency. The PNA has a measurement resolution of 312 KHz. The network analyzer is used to measure the transfer function of the one-port resonator device to determine the resonant frequency. The transfer function, in this case, the ratio of the input RF power and the return power. Before the measurements, the PNA was calibrated using short-open-load-thru calibration (SOLT). The Agilent 8505C APC7 calibration standards were used. The ammonia gas was supplied to the testing chamber using a Unit UFC 1100A mass flow controller (MFC), which was calibrated by Coastal Instruments for 0-11 sccm. The 15 Volt MKS PR4000-F2V1N power supply was used to provide voltage control to the MFC. The MFC flow rate was varied to minimize errors due to the time delay from the MFC reaching the desired flow rate and minimize the filling time. Lastly, the chamber was vented of ammonia by removing its lid and allowing the fume hood to remove the gas.

To ensure accuracy in this experiment, it is necessary that the surrounding area be movement-free. The experiment set up using a mass flow controller ensures the accuracy in determining the amount of gasses present in the chamber. Previous publications^{40-41, 58-62} relied on the pressure gauge to determine the pressure that was then translated into ppm. The reported method had great uncertainty in determining the amount of gasses present in the testing chamber.

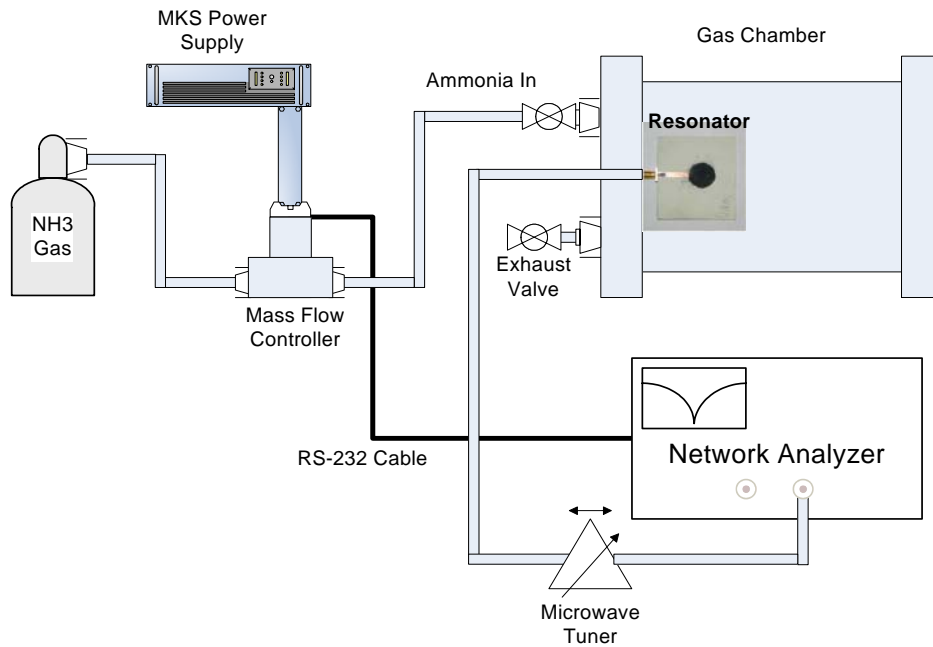


Figure 5. Picture of the experimental set-up

4.3 Experimental Results

The manual impedance tuner was used to match the resonator circuit so that it can achieve a return loss to beyond -40 dB. This low return loss is important in detecting the sensitivity of the resonator sensor. Figure 6 shows the comparison return losses of the 1-port resonator sensor. Upon exposure to ammonia, the resonant frequency shifted to indicate the detection of gasses. When ammonia is removed from the testing chamber, the resonant frequency recovers to its original value. We have also verified that without the carbon nanotube coating, the resonant frequency of the resonator remains unchanged upon exposure

to ammonia, at concentrations below 30,000 ppm. Above this concentration, the pressure increase caused by the ammonia is no longer negligible and the center frequency of the resonator decreases with increasing ammonia concentration (increasing pressure). This experiment confirms that the carbon nanotube material enables the sensing capabilities in the microwave resonator. Once we have confirmed that there is a change in the resonant frequency due to the interaction between the ammonia and the carbon nanotubes, we proceeded in conducting experiments to characterize the sensitivity of the microwave resonator sensor.

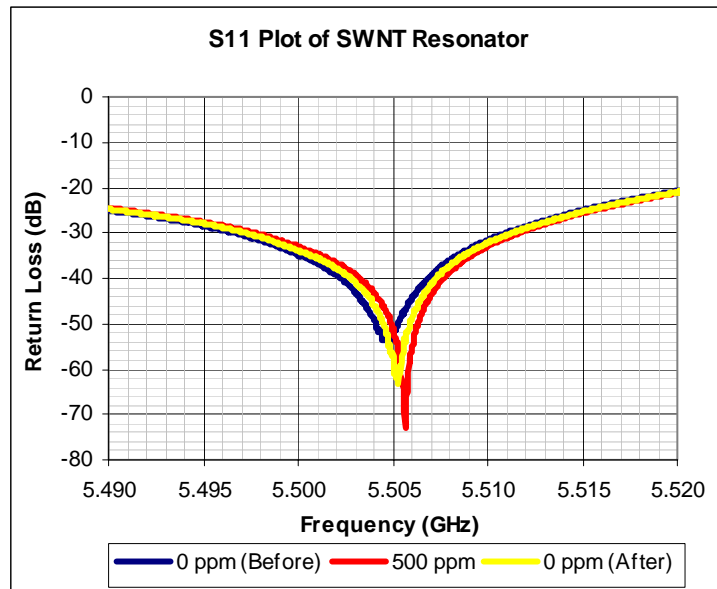


Figure 6. Return losses of the microwave carbon nanotube resonator sensor

To measure the sensitivity, we determined the shift of resonant frequency with respect to the amount of ammonia in the testing chamber. The amount of ammonia flown into the chamber was controlled by a Labview program that allows the response to stabilize. The S-parameters were constantly taken after the response time and a few minutes later. The amount of resonant frequency shift was monitored to be consistent and plotted in Figures 7 and 8. These two figures provide small ppm to demonstrate the working range of the sensor. As seen from Figure 8, the sensitivity of the sensor is very high, up to 4000 Hz/ppm at 100ppm. This is in the order of 1000 times higher than SAW sensor. In addition, the large frequency shift is important in system development to reduce false alarm of the sensor. As the amount of ammonia increases, the sensor still has sensitivity up to 30,000ppm. We

stopped the experiment 30,000 ppm, for these concentrations cause the pressure of the chamber to increase to the extent that it begins to lower the resonant frequency of the sensor. It is more important to achieve high sensitivity at low amount of gasses for sensor applications. Beyond 400ppm, the sensitivity decreases down to 1000 Hz/ppm as shown in Figure 8.

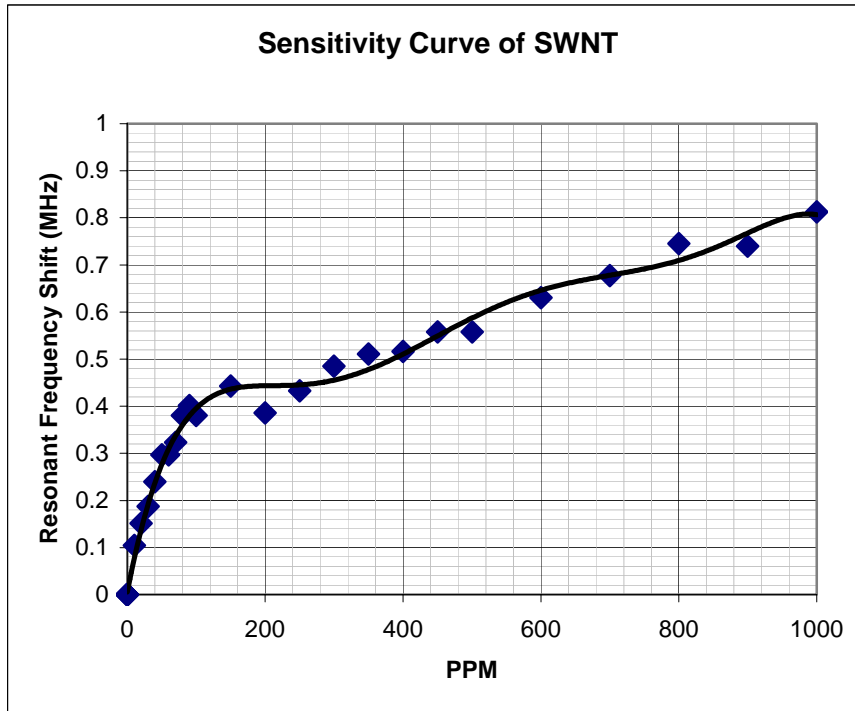


Figure 7. Measured resonant frequency shift versus amount of ammonia at x GHz

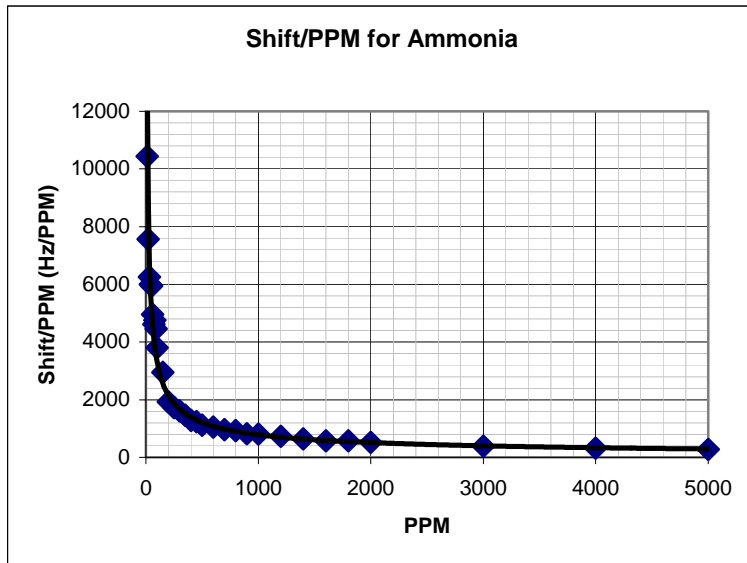


Figure 8. Measured sensitivity (Hz/ppm) of the microwave carbon nanotube resonator sensor.

Simulations were performed to estimate the effect of the permittivity of the nanotube layer on the resonant frequency. The estimate was obtained by performing simulations with Sonnet[®] and CST[®]. Numerous values for the permittivity of the nanotube cover were used, and it was found that for a permittivity of the cover around 5, the approximate average permittivity of the nanotubes, a change in resonant frequency around 1MHz corresponds to a change in the relative permittivity of 0.15. This change was also found to be approximately linear for frequency changes of a few MHz.

Figure 9 shows the response of the sensor as it is alternately cycled between 10,000 ppm and 0ppm ammonia in an ambient environment. Ammonia was introduced into the chamber as described previously, and the sensor response was allowed to settle. After the response had stabilized, ammonia was removed from the chamber by simply removing its lid and allowing the fume hood to evacuate the ammonia. As seen from the plot, the sensor shows a reversible change in the resonant frequency. It is noted that the value of resonant frequency at 10,000 ppm does not increase after several cycles of dry air and ammonia. This result indicates that the resonant frequency shift is highly repeatable and reversible. This translates into a reversible change in the effective dielectric constant of the resonator sensor. It is noted that this plot cannot be used to estimate the response and recovery time since the time it takes to cycle the gas is quite long for this particular testing chamber. It is assumed that the polar ammonia molecules adhere to the sides of the chamber during the response part

of the test, causing the actual concentration to be slightly lower than expected, and these molecules release during the recovery portion of the test, causing observed response time to be longer than the actual response time. However, the results do demonstrate high degree of repeatability.

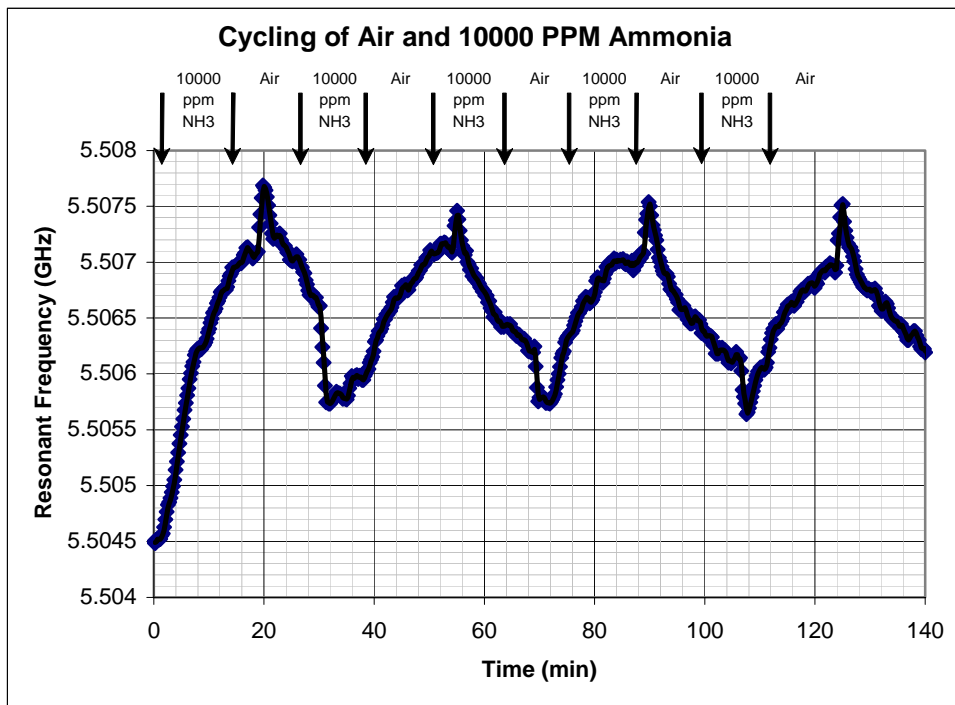


Figure 9. Measured resonant frequency shift when the sensor is cycled between pure ammonia and dry air at 10,000 ppm. The changes are reversible.

Figure 10 shows the response of the sensor as it is alternately cycled between increasing ammonia concentrations and zero concentration in an ambient environment, with an initial ammonia concentration of 100 ppm. The cycling was performed in the same manner as the previous experiment. The results indicate for increasing ammonia cycled with ambient air, the sensor resonant frequency is reversible and its resonant frequency rises with an increase in the ammonia concentration present in the chamber. The sensor can detect

different amount of ammonia with distinct shift and is reversible at different exposure dose.

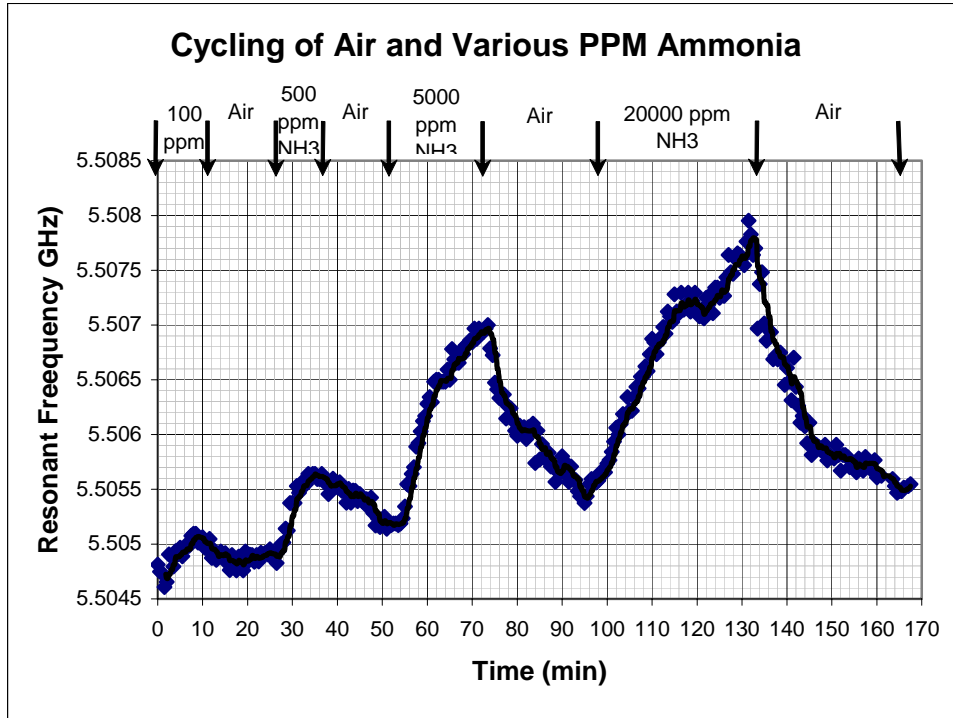


Figure 10. Measured resonant frequency shift when the sensor is cycled between increasing ammonia concentrations and dry air.

4.4 Sensing Mechanism

Certain gas species have been shown to bind to the nanotubes^{38-41, 44-51, 54-56, 58-62}. These gases tend to be oxidizing/reducing agents and also tend transfer charge to the nanotubes. There have been attempts to explain the permittivity change in terms of viewing the absorbed ammonia as having a dielectric constant close to that of its liquid state, 22. Since the dielectric constant of the nanotubes is around 5, it has been proposed that the effect of the absorbed ammonia is to raise the dielectric constant of the nanotube layer by means of an averaging process. However, we have observed an increase in the resonant frequency, which implies that the permittivity of the nanotube cover is decreasing. We have also observed that coating the resonator with a vertically grown multi-walled nanotube array, as oppose to the randomly aligned SWNTS used here, the frequency shift is in the opposite direction. Assuming the dielectric constant of the multiwalled nanotubes is approximately equal to that of the individual tubes, this observation implies another mechanism for the change of the dielectric constant. The results do correlate with the oxidizing/ reducing nature

of the gas and the state of the nanotube coating. Ammonia, a reducing agent, donates electrons to the nanotube⁷¹. Since the single walled nanotube coating is p-type due to the effect of oxygenation^{38, 41}, the donated electrons tend to cancel out the holes and thus reduce the conductivity and permittivity. The vertically grown array of Multi-walled nanotubes yields relatively pristine, defect free, tubes. Since oxygenation has been shown to occur at the defect sites⁴¹, the lack of defect sites indicates the tubes should be virtually intrinsic, so donated electrons increase the conductivity and permittivity. This change in conductivity manifest it self in a change in permittivity. The imaginary part and real parts of the permittivity appear to increase monotonically with conductivity. In reference 72, the permittivity of metallic nanotubes was found to increase proportionally to the square of the Fermi level, with a positive additive term reflecting the increase of carrier concentration with temperature. The results here suggest that for our nanotube coating, consisting of tubes with a wide range of properties, that the carrier density is the dominant factor. Thus, the effect of an increase in conductivity would result in an increase of loss, a decrease in Q, an increase in the effective dielectric constant, and an increase in the resonant frequency. A decrease in conductivity should cause the opposite effect.

V. Wireless Sensing Efforts

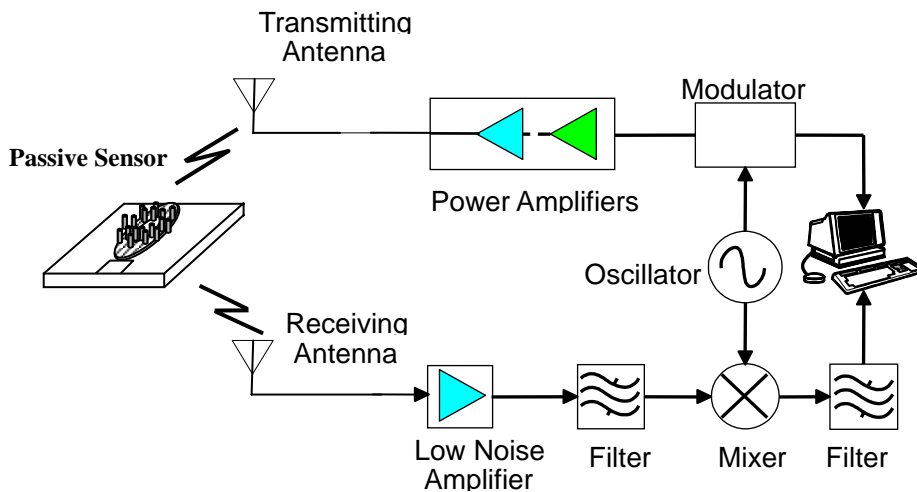


Figure 11. Illustration of wireless sensor system.

Wireless sensors have been implemented in various ways. Two main categories of the passive variety are continuous and pulsed interrogation. Pulsed interrogation involves

pulsing the interrogation signal. The signal would interact with the sensor and be reflected back. When this signal reaches the receiver, the interrogating signal will be turned off. The received signal would be that of the original signal, but it will have undergone amplitude and phase variations. These variations will contain the information to be monitored. Demonstrations have used FM signals to interrogate the sensor in this pulsed manner, by mixing the interrogating signal with the received signal and using the output (containing information of the phase shift) to quantify the parameter to be sensed. Varadan has used an additional antenna on the sensor to serve as reference to eliminate the interference caused by the differences in sensor location from the interrogator. This method is limited to high Q sensing devices. Devices must be able to store energy for relatively long periods of time, thus decreasing the switching speeds required for transmitter/receiver system. SAW are capable of this kind of interrogation⁷³. Spectral domain sensors are not suited for this kind of interrogation in a cost efficient manner, for the required switching times are very short.

The other type of interrogation is characterized by a continuous interrogating signal. Kong et al have demonstrated this with carbon nanotube coated LC-tank sensor by monitoring the impedance of a loop antenna in the vicinity of the sensor with an impedance analyzer⁵⁶. Similar results have been obtained by Yoon, with FM modulation of the interrogating signal⁵⁵. Although this has been shown to work, it is very sensitive on the location of the sensor, as well as other factors. The ideal situation would be to modulate the information onto the carrier signal at the sensor itself.

VI. Carbon Nanotube Functionalization Efforts

Although nanotubes have been shown here to be significantly sensitive to Ammonia, as well as NO₂ and other toxic substances elsewhere, many substances that are of interest do not react significantly with the intrinsic nanotubes. Also, it is also desirable to increase sensitivity, selectivity, increase response time, and decrease recovery time. Many efforts are underway to try to address these. Nanotubes have been functionalized by various means for different applications⁷⁴⁻⁸². Specifically, for the application of gas sensors, numerous attempts have been made. Nanotubes doped with nitrogen (CN_x tubes) have been used in conductivity sensors and have shown responses to relatively high concentrations (>1%) of ammonia, acetone, ethanol, gasoline, pyridine, and chloroform⁷⁴. Nanotubes have been doped with poly-m-aminobenzene sulfonic acid for use in a conductivity sensor, resulting in a reported two-fold increase in sensitivity to ammonia⁷⁶. Tin Oxide coatings of 1-6nm have also been

reported for nanotubes^{75, 77}. Sensors have been constructed with these structures with responses for ppm concentrations of NO, NO₂, ethanal, and C₂H₂. Nanotubes have been used in conjunction with a Pd thin film for hydrogen detection with some success⁷⁸. Doping nanotubes with Pd has been demonstrated to be very effective, with sensitivities to .5% H₂ in a nitrogen environment⁷⁹. However, these tin oxide and palladium functionalized sensors do require temperatures in excess of 200 C⁰. Amidoferrocenyl-functionalized nanotubes have been demonstrated to recognize the presence of mM concentrations of H₂PO₄⁻ at room temperature⁸². Unfortunately, it appears that the gas selective nature of the metal oxides can not be combined with the room temperature operation of the nanotubes, but room temperature responses have been observed for 6ppm of methanol with Pd loaded carbon nanotubes⁶⁸. Peng and Cho have shown the possible detection of CO with carbon nanotubes doped with boron and nitrogen, and they have also suggested that sensitivity can be controlled through doping⁶⁷. Further research is needed to see if other molecules could be used to aid selective reactivity at room temperature and ambient conditions. It has also been shown that the charge transfer to nanotubes depends on their chirality, and that metallic tubes have the fastest rate of charge transfer. It was also shown that the smallest band gap tubes have a tenfold increase in their charge transfer rate, implying the ability to tune response/recovery times⁸³. Although constructing a layer of tubes of a single chirality is a daunting task, chiral selective charge transfer offers hope in improving our ability to select tubes of specific properties in the future.

VII. Future Research

Our research efforts are focused on providing a robust wireless sensor node with tunable selectivity. Wireless sensing has been demonstrated, but there is still progress to be made to do it in a reliable, cost efficient way. Our current research regarding the wireless aspect of this project involves reducing the sensitivity of the wireless node to its environment, while increasing its sensitivity with respect to the species to be detected. The main challenge for the wireless aspect of the node to be overcome is to modulate the information regarding the concentration of the detected species on the sensor itself, eliminating the sensitivity to the sensors position, while doing so in a way that allows us to reduce the temperature sensitivity to a negligible amount. Also, we are investigating ways in which to make the carbon nanotubes a suitable transducer for a wider range of species through fictionalization and increasing its selectivity either through fictionalization or mass selective polymer coatings.

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