Development of RF Carbon Nanotube Resonant Circuit Sensors for Gas Remote Sensing Applications

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Abstract **– We present the design, development and analysis of highly sensitive and ultra-fast responsive electromagnetic microwave resonant sensors for monitoring the presence of gas. These novel sensors consist of circular electromagnetic resonant circuits coated with single and multi walled carbon nanotubes (SWNT & MWNT) that are highly sensitive to adsorbed gas molecules. Upon exposure to ammonia, the electrical resonant frequency of the sensor exhibits a frequency shift of as high as 6.25 MHz. The recovery and response times of these sensors is nominally 10 minutes when operating at room temperatures. This sensor technology is suitable for designing remote sensing systems to monitor gases inside sealed opaque packages and for environmental conditions that do not allow physical wire connections.**

I. INTRODUCTION

Gas sensors can be used in a variety of applications ranging fromdomestic gas alarms and medical diagnostic apparatus to safety, environmental and chemical plant instrumentation [1]. Some of the sensor materials, which have been demonstrated, include semi-conducting metal oxides [2], silicon devices [3, 4], organic materials [5, 6] and carbon black polymer composites [7]. The most common electrical gas sensors are solid state and electrochemical devices, which are known to be inexpensive and safe. Solid electrolytes and semiconducting metal oxides have also been used for gas sensing and have very high sensitivity. The high sensitivity of these sensors is enabled by operating them at high temperatures (200° to 600° C) to achieve enhanced chemical reactivity between the sensor materials and the gas molecules [8, 9]. Plastic film sensors have been demonstrated for ammonia detection and have showed excellent response and recovery times but detection is done in liquid state, which makes it difficult to use in remote sensing applications [10]. Conducting polymers and organic phthalocyanine semiconductors have also been investigated for sensing NH_3. The former exhibits limited sensitivity whereas the latter tend to have very high resistivity (sample resistance of $>10\,G\Omega$) [11]. Also, these sensor technologies require direct physical connections, which limit their applications in sealed environments such as food packages and packages of medicine.

In this paper, we present the development of novel resonant-circuit sensors coated with carbon nanotubes. These sensors operate at room temperatures, exhibit sensitivity to ammonia concentrations as low as 100 ppm, and have response and recovery times of 10 minutes. These sensors respond to ammonia gas by a change in their resonant frequency as a result of interaction of adsorbed ammonia molecules with the carbon nanotubes. The change of resonant frequency can be easily detected using a radio frequency (RF) receiver that will enable the design of a remote sensing system.

II. REMOTE SENSING SYSTEM

Fig. 1 demonstrates the schematic block diagram of a remote sensing system that utilizes a RF wireless transceiver. This system monitors the presence of gas by transmitting and receiving signals through two single turn loop antennas [12]. The interrogation region can be thought of as the region around the sensor where it can detect the change in the concentrations of gases. A signal is sent through the modulator via the power amplifier to the transmitting antenna. This signal interacts with the sensor at the site of detection and is detected by a receiving antenna. The resonant frequency is then compared with the originally transmitted frequency to discriminate the presence of gas. The key component in this system is a carbon nanotube resonant circuit that changes its resonant frequency in the presence of gases.

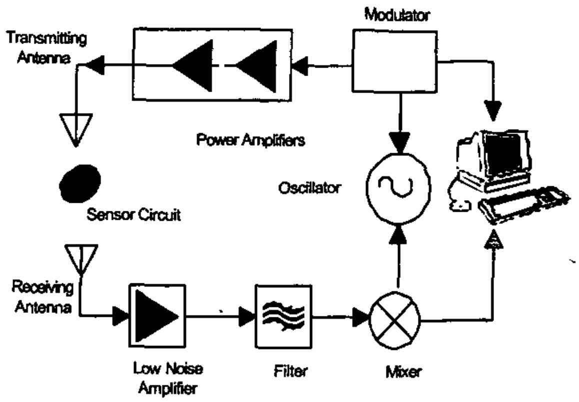

Fig.1 Schematic drawing of a remote wireless sensor system

III. DESIGN OF SENSOR CIRCUIT

A circular disk resonator that has an electrical resonant frequency in the GHz range has been employed in this work. The device comprises a conductor circular disk that is directly integrated on top of a dielectric substrate where the electromagnetic energy is stored. As has been shown by Watkins [13], the resonant frequency f_r of the resonator model with magnetic walls at $r = r_0$ can be approximated by

$$\omega = \frac{1.841c}{a\sqrt{\varepsilon_r}} \qquad (1)$$

where $c = 3\times10^{10}$ cm/s is the speed of light; a is the radius of the circular disk; ε_r is the relative dielectric constant of the substrate. The dominant mode is designated as the TM_{110} mode. The actual resonant frequency of the disk resonator is lower than that predicted by the simple approximate theory used above. However, electromagnetic simulations can be used to optimize for the desired resonant frequency.

Using equation (1), the radius of a 4GHz resonator is calculated using a relative dielectric constant $\varepsilon_r = 3.3$ and a board thickness of 60 mils for the Roger RO4003 board. This resonator is fed by a microstrip line that capacitively couples the energy in a 1 port device configuration. The simulations have been conducted on HFSS (High Frequency Structure Simulator) to design the microstrip feed line and to ensure the resonant frequency. The actual prototype of the resonator is developed using a milling machine that selectively etches the copper conductor on a Duroid board. Single walled and multi walled carbon nano-tubes are physically coated on top of the conducting disks of copper on the face of the resonators using conductive epoxy. Carbon nanotubes are cylindrical molecules with a diameter as little as 1 nanometer and a length up to many micrometers. They consist of only carbon atoms, and can essentially be thought of as a single layer of graphite that has been wrapped into a cylinder [14]. Thus, two prototypes are prepared, one with SWNT's and the other with MWNT's (Fig. 2 (a)).

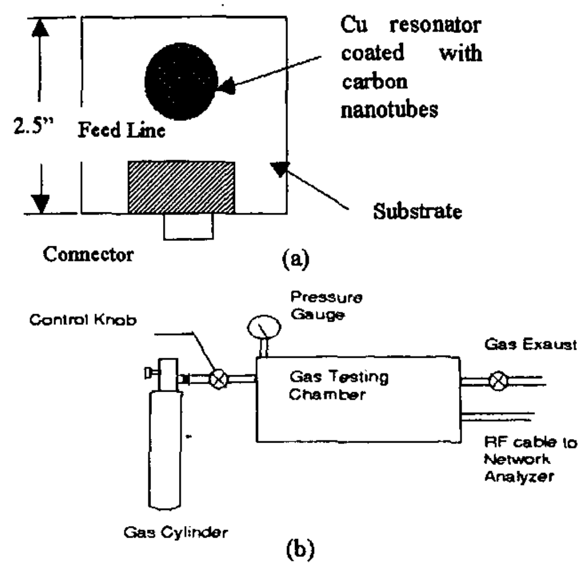

Fig. 2(a) Circular resonator coated with SWNT and MWNT (b) Schematic representation of the testing setup.

The experiments are conducted using an 8753ES-network analyzer that can measure the return loss of a microwave resonator. The prototypes are placed inside an airtight chamber and air is evacuated to achieve vacuum (Fig 2(b)). The return loss is measured every 10 minutes after supplying ammonia into the cylinder and monitoring the pressure with a standard pressure gauge. In a one port device, the return loss provides the transfer function for the ratio of input to return power waves. The resonant frequency is determined at the return loss dip. The recovery time is determined by releasing the ammonia and monitoring the resonant frequency returning to its original value. The recovery time is observed to be 10 minutes for these resonant sensors coated with carbon nanotubes.

III. RESULTS

Fig. 3 demonstrates the measured resonant frequencies of the SWNT sensor under different environmental conditions. The first is the measurement of return loss in vacuum with the resonant frequency being 3.895625 GHz. After the sensor is exposed to

649.27 ppm of ammonia, the resonant frequency changes by 4.375 MHz, shifting the resonant frequency to 3.87125 GHz. Then the chamber is pulled down to vacuum again and the resonant frequency shifts back to 3.895625 GHz. The response time of this sensor is 10 minutes, which is comparable to 10 minutes for other gas sensors [10]. The time in which the resonant frequency of the sensor returns to its original value after the evacuation of ammonia is the recovery time. For this sensor the recovery time is 10 minutes, which is better than other reported sensors having recovery times of 8-12 hours [10].

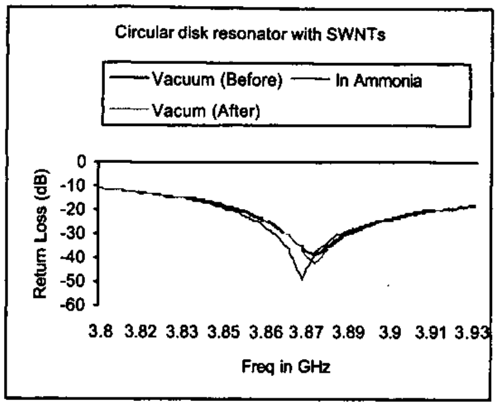

Fig.3 Measured return loss of the SWNT sensor under different environmental conditions

The other resonator has been coated with multi walled carbon nano-tubes all over the entire conducting disk. The same technique is used to perform the measurements of the MWNT sensors. Fig. 4 demonstrates the measured resonant frequencies of MWNT sensors under different environmental gases. The resonant frequency of the MWNT sensor under vacuum is 3.805625 GHz. When exposing to NH_3, the resonant frequency changes to 3.8925 GHz, which results in a frequency shift of 3.125 MHz. The shift in the resonant frequency of the MWNT sensor is less than that of the SWNT sensor. This indicates that the SWNT sensor is much more sensitive to interactions with gas molecules adsorbed on the surface of SWNTs.

Another set of measurements has been performed on the same sensor circuits using the same procedure but with oxygen in place of ammonia. When these sensors are exposed to oxygen, the resonant frequency doesn't change. This behavior can be attributed to the presence of oxygen molecules on the sensor surface even before the exposure to pure oxygen, due to their interaction with air [15]. This helps in the detection of ammonia in the atmosphere, where ammonia is diffused within air.

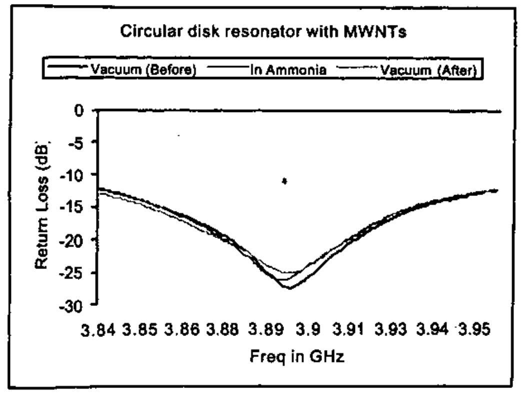

Fig.4 Measured return loss of MWNT sensor under different environment conditions

In Fig. 5, we compare the sensitivity of both devices with respect to the amount of ammonia present in the chamber. It can be seen after curve fitting that these sensors show exponential behavior. The experimental results demonstrate that the sensors are sensitive to concentrations of ammonia as low as 92.69 ppm and the maximum shift in frequency is 6.25 MHz. To the best of our knowledge, these types of resonant sensors provide the best sensitivity or the frequency shift that can be used in electromagnetic remote sensor systems. The frequency shift of 6.25 MHz is about eight times higher than 800 kHz, which contemporary sensors can produce to date [11].

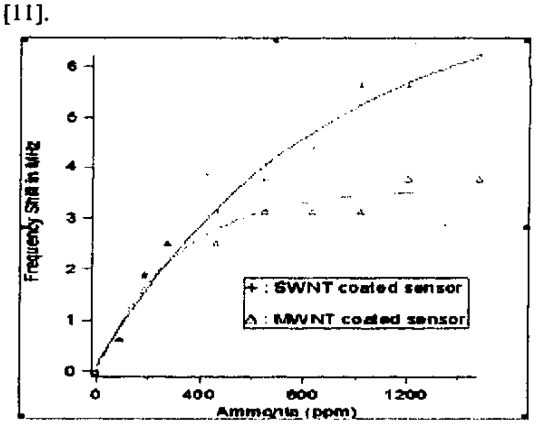

Fig. 5 The comparison of sensitivities of the SWNT and the MWNT resonator sensors

IV. ANALYSIS

It has been demonstrated that the electrical conductance of SWNT's decreases drastically when exposed to NH_3 [10]. However, electromagnetic simulations show that changes in conductivity of resonator disk do not result in a resonant frequency shift of an electromagnetic resonator. The resonant frequency shift can be attributed to the increase or decrease of the effective dielectric constant of heterogeneous materials. In this circular disk resonator, the dielectric materials that influence the electromagnetic fields are Duroid, air, and carbon nanotubes. The effective dielectric constant is a value that represents the combined dielectric constants of the three materials in the planar circular disk resonator. Hence, changes in the dielectric constant of carbon nanotubes will result in the changes in the effective dielectric constant that will cause a shift in resonant frequency of the resonator. From the measurements done above and equation (1), a dielectric constant for carbon nanotubes can be estimated. Then, a circular disk simulation model is constructed in HFSS to include a thin layer of dielectric material on top of the conducting disk. The dielectric constant of this dielectric layer is varied while monitoring the changes in resonant frequency. The electromagnetic simulations of this structure confirm that the frequency shift can be attributed to the changes of the dielectric constant of carbon nanotubes. Also, the resonant frequency is shifted downward or upward with respect to increase or decrease of the dielectric constant of the thin dielectric layer on top of the circular disk, respectively. In the resonator coated with carbon nanotubes, the dielectric constant of the carbon nanotubes is believed to have changed upon exposure to NH_3. A possible explanation is that the NH_3 molecules have interacted with carbon molecules on the face of the carbon nanotubes. This interaction may create bound charges that consist of nitrogen and carbon atoms on the surface of carbon nanotubes. These bound charges change the polarization charge distributions that result in changes in the dielectric constant of carbon nanotubes.

V. CONCLUSION

In this paper, we report the development of microwave resonant sensors coated with carbon nanotubes for detection of gases. To date, these types of resonant sensors provide the best frequency shift or sensitivity when exposed to ammonia. These sensors can be used in microwave remote sensing systems that monitor the changes in frequency shifts to detect the presence of gases. These sensor systems are important in applications that prohibit the use of physical connections, require non-destructive testing or limit the use of sensors at room temperatures. Also this work represents pioneering applications of carbon nanotubes in high frequency electronic circuits and sensors.

VI. ACKNOLEGEMENTS

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VII. REFERENCES

[1] Joseph Watson and Kousuke Ihokura, "Gas Sensing Materials", *MRS Bulletin*, pp.14-15, June 1999.
[2] Y. Shimizu and M. Egashira, "Basic aspects and challenges of Semiconductor Gas Sensors", *MRS Bulletin*, vol. 24, pp.18-24, (June 1999).
[3] H. M. McConnel et al, Science, vol. 257, pp. 1906, 1992.
[4] A Mandells and C Christophides, "Physics, Chemistry and Technology of Solid State Gas Sensor Devices" (Wiley, New York, 1993).
[5] J. Mlasik, A. Hooper, B. Tofield, *J. Chem Soc Faraday Trans.*,vol 1117, pp. 82, 1986.
[6] S. Capone, S Mongelli, R Rella, P. Sicillano, L Valli, Langumir, vol. 1798, pp.15, 1999.
[7] M C Lonergan, E J Severin, B J Doleman, S A Beaber, R H Grubbs, and N. S. Lewis, "Array-Based Sensing Using Chemically Sensitive, Carbon Black-Polymer Resistors", *Chem. Mat.*, vol. 8, pp. 2298, 1996.
[8] Y Takao, K Miyazaki, Y Shimizo, M. Egashira, 'High Ammonia Sensitive Semiconductor Gas Sensors with Double-Layer Structure and Interface Electrodes", *J Elecrochem. Soc.* vol. 141, No. 4, pp. 1028-1034, 1994.
[9] Noboru Yamazoe and Norio Miura, "Gas Sensors Using Solid Electrolytes", *MRS Bull.*, vol. 24, pp. 37, 1999.
[10] H.N. McMurray and J. Albadran, "Colorimetric and Fluorimetric Polymer Membrane Gas-Sensing", *MRS Bull.*, vol. 24, pp. 55, 1999.
[11] Jing Kong, Nathan R. Franklin, Chongwu Zhou, Michael G. Chapline, Shu Peng, Kyeongjae Cho, Hongjie Dai, "Nanotube Molecular Wires as Chemical Sensors", *Science*, vol. 287, pp. 622-625, 2000.
[12] Keat Ghee Ong and Craig A Grimes, "A resonant printed-circuit sensor for remote query monitoring of environmental parameters", *Smart Mater. Struct.*, vol. 9, pp. 421-428, 2000.
[13] J. Watkins, "Circular resonant structures in microstrip", *Electron. Lett.*, vol. 5, pp. 524, 1969.
[14] Cees Dekker, "Quantum Nanotubes As Molecular Quantum Wires", *Physics Today*, vol. 52, pp. 22-28, May 1999.
[15] O.K. Varghese et al, "Gas sensing characteristics of multi-walled carbon nanotubes", *Sensors and Actuators B*, vol. 81, pp. 32-41, 2001.