

Carbon-nanotube-based resonant-circuit sensor for ammonia

S. Chopra and A. Pham^{a)}

Department of Electrical and Computer Engineering, 308 Fluor Daniel Building, Clemson University, Clemson, South Carolina 29634

J. Gaillard, A. Parker, and A. M. Rao

Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634

(Received 4 February 2002; accepted for publication 23 April 2002)

We present the design and development of highly sensitive and fast-responsive microwave resonant sensors for monitoring the presence of ammonia gas. The sensor consists of a circular disk electromagnetic resonant circuit coated with either single- or multiwalled carbon nanotubes that are highly sensitive to adsorbed gas molecules. Upon exposure to ammonia, the electrical resonant frequency of the sensor exhibits a dramatic downshift of 4.375 MHz. The recovery and response times of these sensors are nominally 10 min. This technology is suitable for designing remote sensor systems to monitor gases inside sealed opaque packages and environmental conditions that do not allow physical wire connections. © 2002 American Institute of Physics.

[DOI: 10.1063/1.1486481]

Gas sensors can be used in a variety of applications ranging from domestic gas alarms and medical diagnostic apparatus to safety, environmental, and chemical plant instrumentation.¹ Some of the sensor materials that have been demonstrated include semiconducting 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 (200–600 °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 NH₃. The former exhibit limited sensitivity, whereas the latter tend to have very high resistivity (sample resistance of >10 GΩ).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 letter, we present the development of resonant-circuit sensors coated with carbon nanotubes. These sensors operate at room temperature, exhibit sensitivity to ammonia concentrations as low as ~100 ppm, and have response and recovery times as low as 10 min. 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.

In a remote sensing system, a RF transmitter will send a

microwave signal to the interrogation region, which can be thought of as the region around the sensor where it can detect the presence of gases such as NH₃. The microwave signal interacts with the sensor resonator and produces a strong signal at its resonant frequency. This resonant frequency will be shifted away from the frequency of the transmitted signal in the presence of NH₃. The antenna of a RF receiver is set up to detect the signal at resonant frequencies from the resonator. The received signal is compared with the transmitted microwave signal to resolve the shift in frequency as an indication of the presence of gas. The key component of this system is the circular disk resonator coated with carbon nanotubes.

The sensor is designed using a simple microstrip circular disk resonator coated with carbon nanotubes on the surface of the conducting disk [Fig. 1(a)]. The prototype of the resonator is developed using a milling machine that selectively

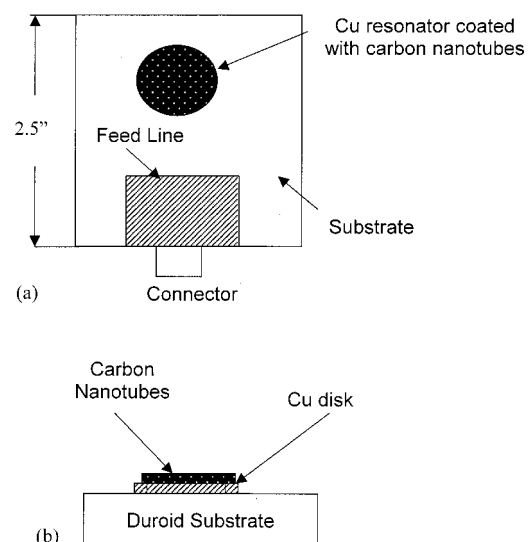


FIG. 1. (a) Schematic of the resonator sensor used in this study. The shaded regions represent copper metal on which the nanotube coating is applied. (b) Cross-sectional view of the resonator sensor.

^{a)}Electronic mail: apham@clemson.edu

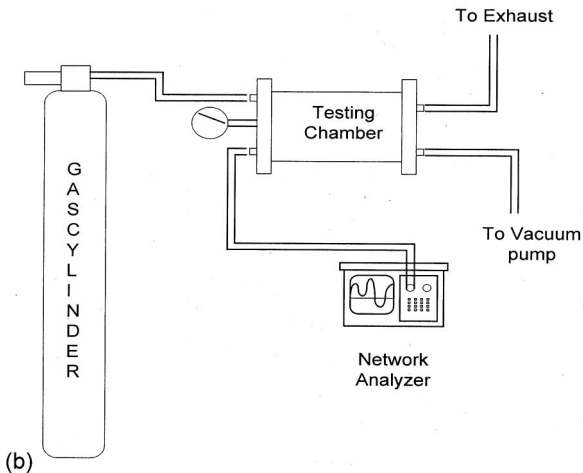
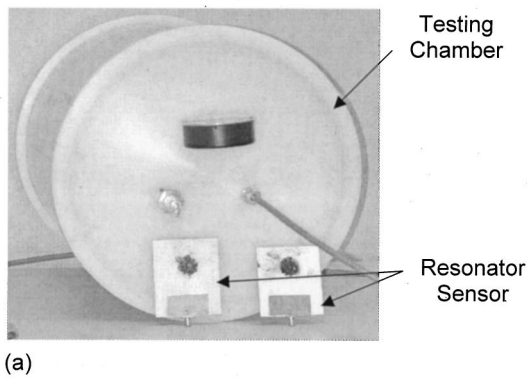


FIG. 2. (a) Prototype of the sensor. (b) Schematic diagram of the testing setup.

etches the copper conductor on a Duroid board. The diameter of the disk is determined by

$$\omega_0 = \frac{1.841c}{\sqrt{\epsilon_r}a}, \tag{1}$$

where $c=3 \times 10^{10}$ cm/s is the speed of light, a is the radius of the circular disk, and ϵ_r is the relative dielectric constant of the Duroid substrate.^{12,13} The actual resonant frequency of the disk resonator will be lower than that predicted by the simple approximate relation used above. However, electromagnetic simulation can be used to optimize the disk diameter for a desired resonant frequency. Using Eq. (1), the radius of a 4 GHz resonator is calculated using $\epsilon_r=3.37$, and board thickness of 60 mils for the Roger RO4003 Duroid board. This resonator is fed by a microstrip line that capacitively couples the energy in a one-port device configuration. A 3.5 mm connector is soldered to the microstrip line for signal detection. The simulations are conducted using a high frequency structure simulator (HFSS) to design the microstrip feed line and to ensure the resonant frequency of 4 GHz. Single- or multiwalled nanotubes (SWNTs or MWNTs) are physically coated (thickness $\sim 5\text{--}10$ and $70\text{--}100$ μm for SWNTs and MWNTs, respectively) on top of the copper disks using conductive epoxy (Circuit Works CW2400). The lengths of the nanotubes in the SWNT and MWNT samples were of the order of several microns with tube diameters of ~ 1.4 and ~ 25 nm, respectively. The resonator sensor is tested in an evacuable, nonmetallic chamber for various con-

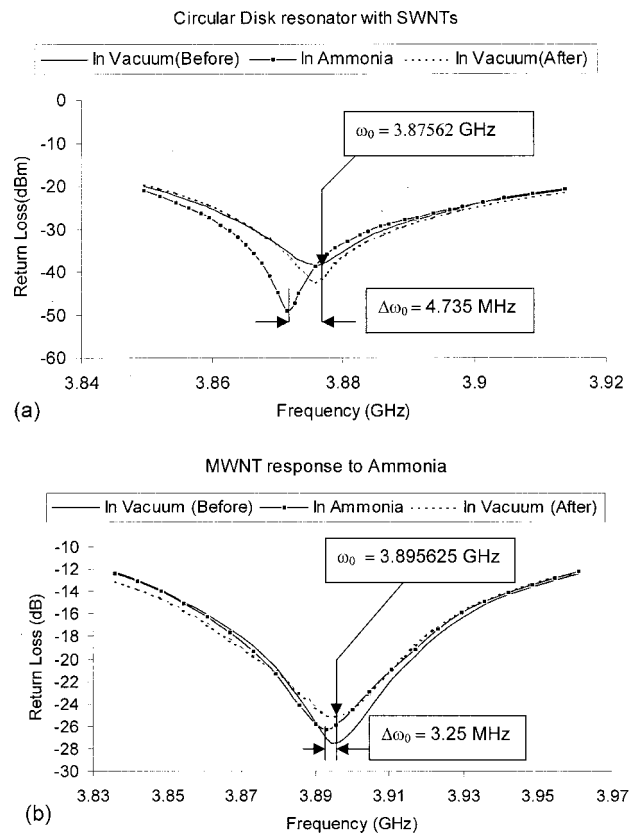


FIG. 3. Measured return loss of the SWNT (a) and MWNT (b) coated sensors vs frequency under different environmental conditions. ω_0 represents the resonant frequency and $\Delta\omega_0$ represents the shift in frequency of the sensor circuit.

centrations of ammonia vapor (Fig. 2). The experiments are conducted using an 8753ES network analyzer that can measure the resonator's return loss to determine the resonant frequency. The number of points in the network analyzer is set to be 1600 to ascertain that the accuracy is 0.0125%.

Figure 3 shows the measured electromagnetic return loss as a function of frequency for the resonant sensors coated with nanotubes under different experimental conditions. The dips in these traces correspond to the sensors' resonant frequency (ω_0). In vacuum (solid traces), ω_0 are 3.87562 and 3.895625 GHz for SWNT and MWNT sensors, respectively. The dotted and dashed traces in Fig. 3 correspond, respectively, to the responses in the presence of ammonia (834 ppm) and subsequent removal of ammonia from the chamber. Clearly, ω_0 of the SWNT sensor changes by 4.375 MHz upon exposure to ammonia for approximately 10 min. A relatively smaller downshift of 3.25 MHz is observed for the MWNT sensor. It has also been ascertained that our circular disk resonators, without the nanotube coating, do not exhibit a change in frequency response when exposed to ammonia.

The response time of 10 min is comparable to that reported for other gas sensors.¹¹ However, the time in which our sensors regain their original resonant frequencies after the evacuation of ammonia from the chamber is approximately 10 min, which is much faster, compared to other NH_3 sensors.¹¹ For example, SWNT chemical sensors based on resistance changes¹¹ exhibit a fast response (a few minutes) with a slow recovery time (8–12 h) under exposure to 200 ppm of NO_2 .

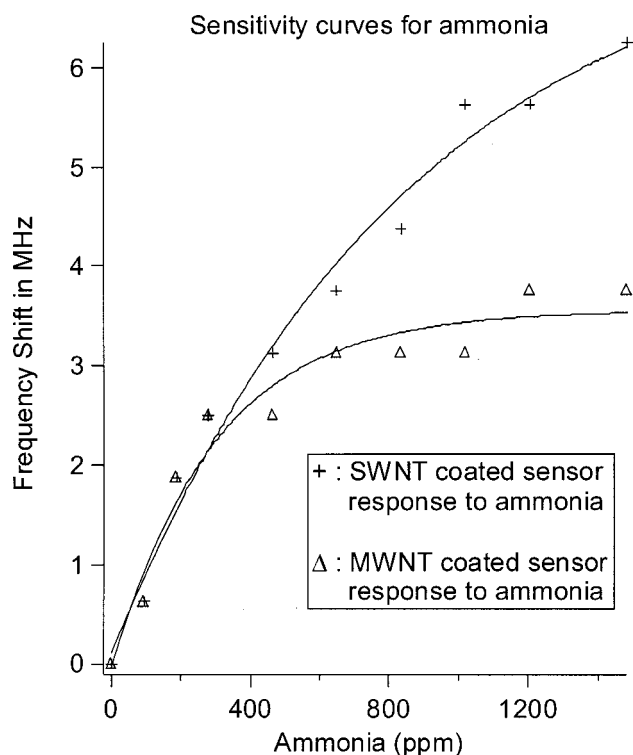


FIG. 4. Comparison between the sensitivities of SWNT and MWNT coated sensors.

The sensors used in this study also provide better sensitivity (or the frequency shift) as compared to these types of resonant frequency detection sensors and are at least five times more sensitive than the recently reported humidity sensor based on a frequency shift mechanism.¹⁴ Figure 4 demonstrates the sensitivity comparison of the resonators coated with SWNTs and MWNTs. The data in Fig. 4 are obtained by gradually exposing the SWNT- or MWNT-coated sensors to a controlled amount of ammonia. The SWNT sensor is more sensitive than the MWNT sensor (Fig. 4) and this observation is consistent with the fact that SWNTs exhibit more capacity for hydrogen storage than MWNTs.¹⁵

We now explain the observed downshift in ω_0 upon exposure of our sensors to ammonia. It has been demonstrated that the electrical conductance of the SWNTs decreases drastically when exposed to NH_3 .¹¹ However, electromagnetic simulations show that changes in conductivity of the resonator disk do not result in a resonant frequency shift of an electromagnetic resonator. The resonant frequency shift can be attributed to the changes in the effective dielectric constant of the heterogeneous materials. In this circular disk resonator, the dielectric materials that influence the electromagnetic fields are the Duroid board and the NH_3 -nanotube system. 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 the carbon nanotubes will result in the changes in the effective dielectric constant that will cause a shift in the resonant frequency of the resonator. This frequency shift is independent of the Duroid dielectric sub-

strate. A circular disk simulation model has been constructed to include a thin layer of dielectric material on top of the conducting disk [Fig. 1(b)]. The dielectric constant of this dielectric layer is varied while monitoring the changes in resonant frequency. The electromagnetic simulation of this structure confirms that the resonant frequency is shifted downward or upward with respect to the increase or decrease of the dielectric constant of the thin dielectric layer on top of the circular disk. In the resonators 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 walls and ends of the carbon nanotubes. This interaction may have created bound charges on the surface of the carbon nanotubes resulting in changes in the dielectric constant of the carbon nanotubes. The absorption of gas molecules onto carbon nanotubes is the fundamental mechanism that enables changes in the dielectric constant. This property of carbon nanotubes is attractive for the design of sensors based on changes of the dielectric constants or frequency shifts.

In summary, we report the development of microwave resonant sensors coated with carbon nanotubes for detection of NH_3 . To date, this type of resonant sensors provides the best frequency shift or sensitivity on exposure to ammonia. This type of electromagnetic resonator sensors can be used in microwave remote sensing systems that monitor the changes in frequency shifts to detect gases. The sensor systems are important in applications that prohibit the use of physical connections or require nondestructive testing.

The authors would like to thank Kris McGuire and B. Sadanadan for providing the carbon nanotubes, and S. Fowler and A. Venkateshan for help in taking measurements. This work was supported primarily by funds through the NASA Ames Research Center, ERC-NSF Award No. EEC-9731680.

- ¹J. Watson and K. Ihokura, *MRS Bull.* **24**, 14 (1999).
- ²Y. Shimizu and M. Egashira, *MRS Bull.* **18**, 24 (1999).
- ³H. M. McConnel, J. C. Owicki, J. W. Parce, D. L. Miller, G. T. Baxter, H. G. Wada and S. Pitchford, *Science* **257**, 1906 (1992).
- ⁴A. Mandells and C. Christophides, *Physics, Chemistry, and Technology of Solid-State Gas Sensor Devices* (Wiley, New York, 1993).
- ⁵J. Mlasik, A. Hooper, and B. Tofield, *J. Chem. Soc., Faraday Trans. 1* **82**, 1117 (1986).
- ⁶S. Capone, S. Mongelli, R. Rella, P. Siciliano, and L. Valli, *Langmuir* **15**, 1798 (1999).
- ⁷M. C. Lonergan, E. J. Severin, B. J. Doleman, S. A. Beaber, R. H. Grubbs, and N. S. Lewis, *Chem. Mater.* **2298**, 8 (1996).
- ⁸Y. Takao, K. Miyazaki, Y. Shimizu, and M. Egashira, *J. Electrochem. Soc.* **141**, 1028 (1994).
- ⁹N. Yamazoe and N. Miura, *MRS Bull.* **37**, 24 (1999).
- ¹⁰H. N. McMurray and J. Albadran, *MRS Bull.* **55**, 24 (1999).
- ¹¹J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, and K. Cho, H. Dai, *Science* **622**, 287 (2000).
- ¹²J. Watkins, *Electron. Lett.* **524**, 5 (1969).
- ¹³I. Wolff and N. Knoppik, *IEEE Trans. Microwave Theory Tech.* **MTT-22**, 857 (1974).
- ¹⁴K. G. Ong and C. A. Grimes, *Smart Mater. Struct.* **421**, 9 (2000).
- ¹⁵M. S. Dresselhaus, K. A. Williams, and P. C. Eklund, *MRS Bull.* **24**, 45 (1999).