

## Selective gas detection using a carbon nanotube sensor

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A circular disk resonator is used to study the gas sensing properties of carbon nanotubes. It detects the presence of gases based on the change in the dielectric constant rather than electrical conductivity of single walled carbon nanotubes (SWNTs) upon gas exposure. A conducting circular disk is coated with electric arc prepared SWNTs and degassed by heating under a high vacuum. It exhibits noticeable shifts in resonant frequency to both polar (NH<sub>3</sub> and CO) and nonpolar gases (He, Ar, N<sub>2</sub>, and O<sub>2</sub>). Gas concentrations as low as 100 ppm can be detected using this sensor configuration. © 2003 American Institute of Physics. [DOI: 10.1063/1.1610251]

Gas sensors play an important role in the industry for controlling manufacturing processes. They are used in a wide variety of applications ranging from domestic gas alarms to environment safety. Traditionally, gas sensors are made using semiconducting oxides as the sensing material. The main drawback of using oxide-based gas sensors is that their use in gas sensing is governed by the microfabrication techniques used to build the sensor.<sup>1</sup> This puts a limit on the size and geometry of the sensor. In order to overcome this difficulty, materials are being investigated for gas sensing applications. Carbon nanotubes stand out as a strong candidate for use as a gas sensing material due to their inherent properties like small size (diameter ~1–100 nm), and good electrical and mechanical properties. Another important property of nanotubes which favors their use in gas sensing is their high specific surface area (1580 m<sup>2</sup>/g).<sup>2</sup> Solid-state gas detection results from the adsorption (interaction of gas molecules with the surface) of gas molecules on a material surface. Due to the high specific surface area of nanotubes, little nanotube material can provide ample sites for gas interaction.<sup>3</sup> Hence, nanotubes can serve as an economically viable material for use in gas detection. Another plus is their small size. Due to these reasons, nanotubes have been explored for gas sensing in a number of different configurations.<sup>3–5</sup>

The basic principle behind gas detection is a change in an electrical property of the detecting material upon exposure to the gas. For example, in the case of carbon nanotubes, the resistance changes with exposure to different gases like NO<sub>2</sub> and NH<sub>3</sub>.<sup>4</sup> Other electrical properties of nanotubes like thermoelectric power,<sup>6,7</sup> and dielectric properties<sup>5,8</sup> also change upon gas exposure. These properties of carbon nanotubes change appreciably in the presence of gases. In a previous publication, we studied the change in the permittivity (dielectric behavior) of air-exposed nanotubes upon exposure to NH<sub>3</sub>.<sup>8</sup> It was found that the resonant frequency of single walled nanotubes (SWNT) or multiwalled nanotube-coated disk resonator downshifts upon exposure to few ppm of NH<sub>3</sub> due to a change in dielectric constant of nanotubes, consistent with other gas sensing platforms.<sup>9</sup> No shift in resonant

frequency was observed when the resonator was exposed to inert gases such as He, Ar, or N<sub>2</sub>. In this study, we used an identical disk resonator coated with *degassed* nanotubes to determine whether a measurable shift in the resonant frequency is achieved when exposed to inert gases.

Figure 1 shows the schematic of the prototype used in this experiment. The sensor is designed using a simple microstrip circular disk resonator.<sup>10</sup> Simulations are done on a high-frequency structure simulator to optimize the microstrip dimensions. A Duroid board (Rogers RO4003) is milled to fabricate a circular disk resonator resonating at 4 GHz according to

$$f_0 = \frac{1.841c}{2\pi a\sqrt{\epsilon_r}}, \quad (1)$$

where  $f_0$  is the resonant frequency of the resonator,  $c$  is the speed of light in a vacuum,  $a$  is the radius of the disk, and  $\epsilon_r$  is the relative dielectric constant of the substrate (Duroid board). A 3.5 mm 50  $\Omega$  SMA connector is connected to the input microstrip line to transfer energy to and from the resonator to a vector network analyzer (Model HP 8753ES). SWNTs prepared using an electric arc method (~70% purity) are coated on top of the circular disk using a conductive epoxy (Circuit Works 2400). The lengths of the nanotube bundles in this experiment were of the order of several microns and the dominant tube diameter was ~1.4 nm. The

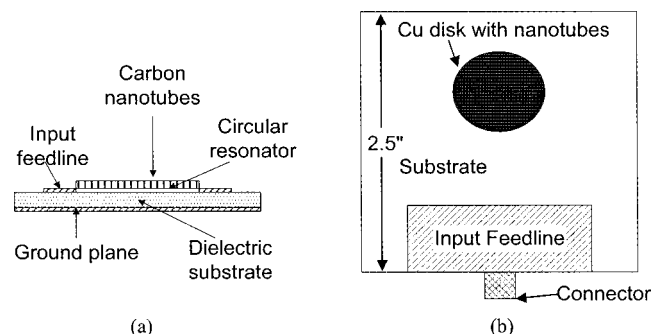


FIG. 1. (a) Schematic of front view of the resonator circuit. (b) Top view of the resonator sample coated with nanotubes.

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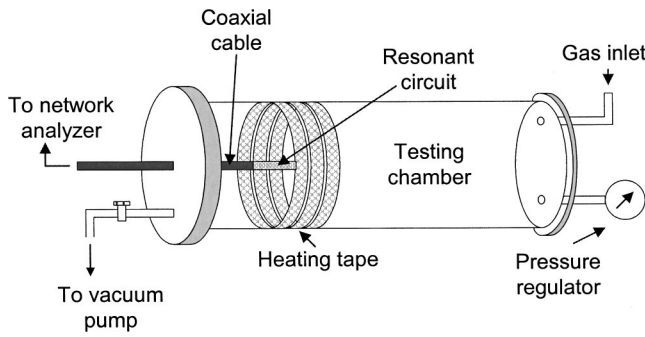


FIG. 2. Schematic of the testing setup.

resonant frequency was determined from the return loss spectrum of the resonator. The resonator is used in a one-port configuration with the same port acting as the input and output.<sup>10</sup> The number of points in the network analyzer spectrum is set to 1600 to give a smallest measurable frequency change of 250 kHz.

Figure 2 shows a schematic of the testing chamber used for testing the sensor response to different gases. The testing chamber is comprised of a glass tube that can be evacuated to a high vacuum ( $\sim 10^{-5}$  Torr) and heated up to 125 °C. These conditions are necessary for degassing the nanotubes coated on the sensor.<sup>7,8</sup> The sensor prototype is placed inside the chamber, evacuated to  $\sim 10^{-5}$  Torr and subsequently heated to  $\sim 125$  °C for  $\sim 12$  h. This process leads to the removal of already adsorbed gas molecules on the nanotube surface (degassing). In Fig. 3, the solid trace shows the response of the sensor prototype with degassed nanotubes and the minima in the trace corresponds to the resonant frequency  $f_0 \sim 3.8893$  GHz. The sensor is then exposed to a known amount ( $\sim 1500$  ppm) of He gas and the response of the sensor is found to stabilize in  $\sim 10$  min. This time is known as the response time and is comparable to the response times reported elsewhere.<sup>4</sup> The resonant frequency shifts to 3.8885 GHz (crosses) with a decrease of 0.8 MHz from the degassed value ( $\Delta f_{\text{He}}$ ) implying that, for degassed nanotubes, even inert gas interactions with the nanotubes affect the dielectric constant of the system. Further,  $f_0 \sim 3.8893$  GHz is completely recovered upon degassing the sensor. A similar response was observed in the temperature dependent thermopower experiments done using degassed SWNT bundles exposed to inert gases.<sup>6</sup> It was concluded that even gas molecular collisions with nanotube walls can contribute significantly to the electrical transport properties.<sup>6</sup>

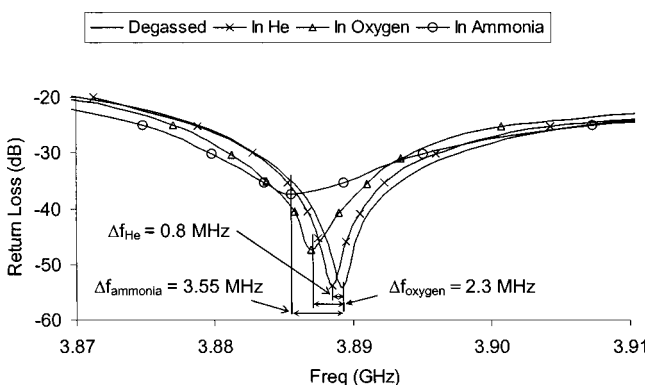


FIG. 3. Response of degassed SWNTs sensor to He and ammonia.

Dielectric Constant & Resonant Frequency Shifts

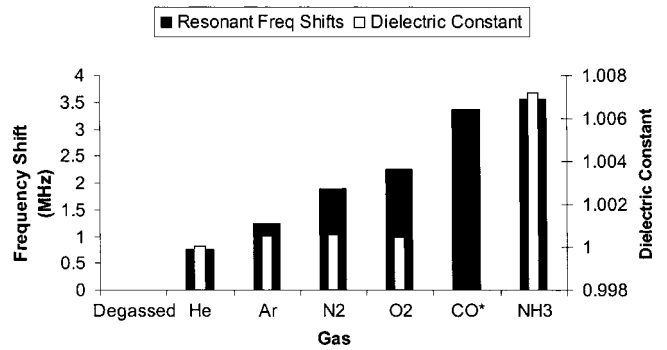


FIG. 4. Resonant frequency shifts (solid bars) and dielectric constants (open bars) of various polar and nonpolar gases. At this point, room temperature value for dielectric constant of CO is not available in the literature.

Upon exposure to oxygen,  $f_0$  shifts to 3.8870 GHz (triangles), giving a resonant frequency downshift ( $\Delta f_{\text{oxygen}}$ ) of 2.3 MHz. This value is the same as the resonant frequency of the sensor in air, indicating that O<sub>2</sub> dominates the behavior of this sensor when exposed to air. The response of the degassed sensor to  $\sim 1500$  ppm of NH<sub>3</sub> is shown by the circles in Fig. 3.<sup>11</sup> We have previously shown that gas concentrations as low as 100 ppm can be detected using this configuration.<sup>8</sup> In this case,  $f_0$  is found to change from 3.8893 GHz to 3.8857 GHz resulting in a frequency downshift of 3.55 MHz ( $\Delta f_{\text{ammonia}}$ ). Thus, we see that our resonator configuration is selective and can detect trace amounts of different gases. Figure 4 shows the measurements of the resonant frequency shifts determined relative to  $f_0$  when the sensor is exposed to air and different gas environments. It should be noted that downshift in  $f_0$  is more significant when the sensor is exposed to a polar gas environment as compared to a nonpolar gas environment. Among the polar gases, ammonia causes a relatively greater shift in  $f_0$  as compared to carbon monoxide. For nonpolar gases, a relatively higher shift is observed upon exposure to oxygen.

It is well known from classical electromagnetics that the resonant frequency of a resonator depends on the dielectric constant of the material [cf. Eq. (1)]. In the present sensor, the effective dielectric constant is a function of the individual dielectric constants of the substrate, conductive epoxy, nanotubes, and the gas present in the vicinity of the sensor. It is a weighted average of the dielectric constant of the nanotubes and the gas present with the weights depending upon factors like adsorption energy and the molecular weight of the gas.<sup>12</sup> In this work, the same sensor was successively exposed to different gases which allowed all of the parameters to remain fixed except for the dielectric constant of the gas under study. Thus, an observed change in  $f_0$  upon a change in the gas type implies a direct correlation between  $\Delta f_{\text{gas}}$ , the dielectric constant of the gas, and the nanotube-gas interactions. The dielectric constant of a gas is given by the Debye equation<sup>13,14</sup>

$$\epsilon = 1 + 4\pi N_1 \left( \alpha_0 + \frac{\mu^2}{3kT} \right), \quad (2)$$

where  $\epsilon$  is the dielectric constant,  $N_1$  is the number of molecules per cm<sup>3</sup>,  $\alpha_0$  is the polarizability per molecule,  $\mu$  is the dipole moment,  $k$  is the Boltzmann's constant, and  $T$  is the

temperature in Kelvin. Since  $\mu=0$  for a nonpolar (and  $\mu \neq 0$  for a polar gas), the dielectric constants of polar and nonpolar gases differ appreciably [cf. Eq. (2)]. This explains why downshifts in  $f_0$  for polar gases are appreciably larger compared to the downshifts for nonpolar gases. Also between ammonia and carbon monoxide, the former has a relatively greater dipole moment and, hence, a greater resonant frequency downshift. In Fig. 4, the right-hand side scale indicates  $\epsilon$  for each gas type used in this study. The downshift in  $f_0$  for nonpolar gases is also proportional to the dielectric constants of the gases with the exception of oxygen (Fig. 4). Based on first-principle calculations, it has been reported that the adsorption energy for oxygen is orders of magnitude greater compared to that for other gases.<sup>15</sup> Hence, the greater downshift in  $f_0$  upon exposure to oxygen may be due to the enhanced adsorption energy of oxygen on nanotubes. These results are summarized in Fig. 4.<sup>16</sup>

In an earlier study using a similar sensor coated with as-prepared nanotubes for the detection of ammonia,  $f_0$  was recovered simply by evacuating the testing chamber.<sup>8</sup> In contrast, when the detection is made using degassed nanotubes as described in this study,  $f_0$  cannot be fully recovered upon evacuation.  $f_0$  could be fully recovered only after the degassing step previously described herein following Fig. 1. This suggests that in the case of a degassed nanotube sensor, few ammonia molecules probably chemisorb on the nanotube surface. Another evident feature in Fig. 3 is the decrease in the  $Q$  factor (loss in conductivity) of the resonator upon exposure to different gases. Interestingly, the  $Q$  factor of the resonator sensor is also not recoverable upon evacuating the gas chamber. This fact concurs with electrical resistivity studies of SWNT-based chemical sensors upon gas exposure.<sup>4</sup> Temperature dependent thermopower studies have also shown that the conductivity of degassed nanotube mats decreases upon exposure to gases.<sup>6</sup> The extent to which this change occurs depends on the nature of the gas and was attributed to the interaction of the gases with the  $\pi$  electrons of the nanotubes.<sup>6</sup>

In summary, a solid-state gas sensor is demonstrated which can be used to detect the presence of a number of

gases ( $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{He}$ ,  $\text{O}_2$ , and  $\text{Ar}$ ). This sensor can detect low concentrations of gases and the response time is small compared to contemporary sensors. This sensor is selective as to the detection of a number of gases giving different resonant frequency shifts to different gases. This sensor circuit can be used in a remote sensing system and can be used for remote sensing in sealed opaque packages.

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