A Novel Highly-Sensitive Antenna-Based "Smart Skin" Gas Sensor Utilizing Carbon Nanotubes and Inkjet Printing

H. Lee*, K. Naishadham, M. M. Tentzeris
Georgia Tech Research Institute/ECE Dept.
Georgia Institute of Technology
Atlanta, Georgia, 30332

G. Shaker
Department of Electrical & Computer Engineering
University of Waterloo
Waterloo, Ontario, Canada N2L 3G1

Abstract – **Carbon nanotubes (CNTs) have attractive features for implementation in wireless sensor nodes due to their small size, light weight and low power requirements, and their ability to be functionalized with conductive polymers for the electronic detection of a range of chemical and biological agents. In this paper, we present a single-walled CNT sensor for gas detection that is printed on paper substrate and integrated with a co-planar RF antenna for potential application as a light-weight wireless sensor node. The CNT thin-film loads the antenna and changes its resonant frequency upon exposure to the gas, the resonant frequency shift then being used as a discriminator for the gas detection in trace quantities. Measurements of a CNT-based sensor when exposed to low levels of ammonia reveal a resonance frequency shift of 300 MHz for a patch antenna centered around 6 GHz. To the authors' knowledge, this is the highest frequency shift reported in literature.**

Keywords-Carbon Nanotubes; Chemical Sensing; Gas Sensors; Power Scavenging; Wireless Sensor Node, Smart Skin

I. INTRODUCTION

Because of their small size, light weight, excellent electrical conductivity, and their ability to be functionalized for enhanced surface adsorption of a wide range of chemicals, carbon nanotubes (CNTs) are ideal materials for the development of a broad spectrum of low-power portable sensors. CNTs have been grown on silicon wafers and integrated with resonant circuit or antenna elements to produce sensors that detect trace amounts of gases such as ammonia, carbon dioxide, etc. [1], [2]. These sensors have been primarily used in laboratory for phenomenological studies, and therefore, require direct interface with an RF source for sensing applications. However, in practice, remote operation of the sensor is needed, which places stringent requirements on the sensitivity, selectivity, and range of the sensor. Also, for rapid deployment in buildings, highways, bridges and other infrastructure, it is desirable to have low-cost sensors that can be powered from thin-film batteries or by power scavenging, and incorporate integration of the sensor and the RF communication device on the same substrate.

In this paper, we report a novel RF sensor comprising a thin-film CNT layer for the detection of ammonia, integrated with a co-planar RF antenna on photographic paper substrate. The antenna metallization is deposited on paper using ink-jet printing of silver inks consisting of nano-particles. We use commercially available single-walled CNTs functionalized with a conductive polymer, polyaminobenzene sulfonic acid (PABS), to enhance the sensitivity to ammonia.

There has been significant work done in CNT-based gas sensors without considering wireless transmission of sensed data. For example, Chopra et al. [1] discuss the design of a patch antenna coated with a mixture of CNTs (in powder form) and a conductive epoxy for ammonia detection. When the CNT coating is exposed to ammonia, it changes the effective permittivity of the antenna and shifts its resonant frequency. The resonant frequency shift relative to the unexposed film determines the presence of the gas. Since the CNT is not functionalized, only 5 MHz shift has been detected even with a high ammonia concentration (1000 ppm). This small shift can lead to false alarms in a wireless configuration, and even antenna manufacturing tolerances can cause such small shifts. The authors in [2] employ a composite of multi-walled CNTs and SiO_2 as a superstrate layer on a planar LC-resonator, and use the change in effective dielectric constant, caused by surface interaction, to detect the gas. The effective permittivity is calculated from the resonator parameters. Due to the small values of inductor and capacitor feasible on silicon, this sensor suffers from low sensitivity too, and the shift in dielectric properties can be masked by measurement errors. Both of these sensors [1], [2] fall into a category of resonant sensors which rely for detection on the shift of *resonant frequency* due to change in dielectric properties caused by CNT loading and its interaction with the gas.

In a second class of gas sensors using CNTs, a shift in *amplitude* is used for the detection. The authors in [8] report experimental results demonstrating change in the modulus and phase of transmitted signal on a micromachined coplanar waveguide (CPW), filled with a mixture of CNTs, when exposed to nitrogen gas. The amplitude resolution of this sensor is only about a dB/cm change in the attenuation constant of the CPW transmission line, and larger than 5 degrees change in phase, from 10 GHz to 100 GHz – too small to be of any utility as a wireless sensor node. Yang et al. [5] load a bow-tie antenna at its feed location with single-walled CNT film and use the change in return loss as a measure of gas detection. This design requires a very high concentration of gas to get a large variation in the loading resistance, and thus suffers from limited sensitivity and slow response detection.

The class of sensors relying on frequency shift is most useful for remote wireless sensing because frequency shift is

easier to detect than amplitude shift even in adverse signal-to-noise conditions. We present a new design incorporating a highly sensitive CNT film that loads a stub connected perpendicular to the radiating edge of a patch antenna, and shifts the resonance frequency significantly upon exposure to ammonia. Without loss of generality, ammonia gas is the example analyte chosen in this study because it is readily available. There are several salient new features of this sensor: (a) unlike [1], [5], the utilized antenna is of high Q, thus of a much enhanced sensitivity, (b) the CNT film is PABS-coated prior to application on the patch for increased sensitivity to ammonia, (c) the antenna can be integrated with RF transceiver to provide duplex communication to a remote platform, and (d) the antenna and the sensor have been printed on paper (also feasible to deposit on liquid crystal polymer or other thin substrates) without using chemical etching, thereby resulting in a low-cost environmentally friendly process for its fabrication. Measurements on the PABS-functionalized CNT sensor reveal a resonance frequency shift of 300 MHz for a patch antenna centered around 6 GHz, the highest frequency shift reported in literature, using only 25 ppm concentration of ammonia.

II. CNT Characterization

Since the CNT film is deposited on photographic paper for the antenna sensor (see Sec. III), we first characterized paper, and then paper with CNT, for their dielectric properties using a rectangular waveguide set-up (Fig. 1). The sample is sandwiched between two calibrated waveguides, and its transmission (or insertion loss) is measured on a network analyzer. The dielectric constant of paper can be calculated using a standard iterative inversion method with measured S21 data. The insertion loss for paper (see Fig. 1), is less than 0.2 dB in the X-band. On the other hand, the second measurement on paper with CNT lowers the transmission coefficient by ~2 dB due to conductive losses in the CNT. Since the latter is a composite of two materials, permittivity of CNT cannot be inverted directly from the measured data. We calculated the complex dielectric constant of paper to be around 3.5 + j0.02 in the X-band (variation was less than 5%). Using this permittivity of paper and the measured S21 of the paper plus CNT combination, we calculated the surface impedance of the CNT film (10 microns thick) using the relation [9]:

$$Z_s = S_{21} Z_0 \frac{\Gamma^2\tau^2 - 1 + \Gamma(\tau^2 - 1)}{2(\Gamma^2 - 1) - 2S_{21}(\Gamma^2\tau^2 - 1)}$$

where Z_0 is the characteristic impedance of the waveguide mode, while Γ and τ are the reflection coefficient and the transmission phase, respectively, for a specified paper thickness, t. These are given by:

$$\Gamma = \frac{\sqrt{\frac{\mu}{\varepsilon}} - 1}{\sqrt{\frac{\mu}{\varepsilon}} + 1} \quad \text{and} \quad \tau = e^{-ik_0 t\sqrt{\mu\varepsilon}}$$

Where, Γ is the reflection coefficient at the air/substrate interface, τ is the transmission coefficient, ε, μ are permittivity and permeability, respectively.

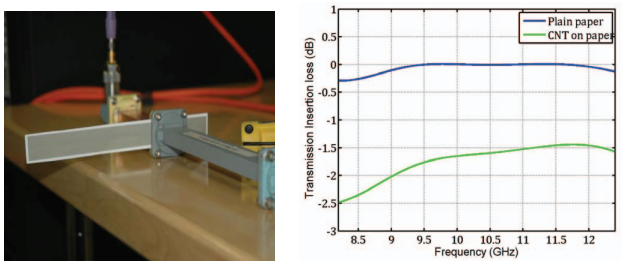


Fig.1. (a) Waveguide set-up used to characterize CNT on paper. (b) Measured insertion loss.

The calculated surface impedance of the CNT film is depicted in Fig. 2. The fluctuations are attributed to the air-gap between the specimen and the waveguide, which is likely to cause errors, particularly with thin conductive specimens. Also, we had difficulty performing TRL calibration in the waveguide and conducted only a response calibration instead. We plan to mitigate these errors in the future by performing transmission line measurements directly on the CNT/paper sample, employing TRL calibration standards specifically constructed for the CNT conductor geometry. For the sensor design in this paper, we assume that paper is characterized by a dielectric constant of 3.5 and the CNT, by a surface impedance of (300 + j100) ohms per square, at 6 GHz, the design frequency of the sensor. The CNT impedance is obtained from Fig. 2 by smoothing the data using a linear fit, and extrapolating the result down to 6 GHz.

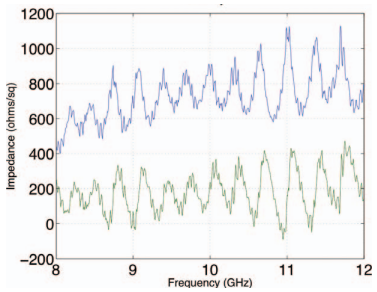


Fig. 2. Surface impedance of the CNT film (top curve denotes the real part and the bottom is the imaginary part).

III. Sensor Design

In order to achieve maximum sensitivity, the patch antenna topology was chosen due to its moderately high Q, and thus narrow bandwidth characteristics. With a higher Q, it is easier to detect the shift in frequency caused by the interaction between ammonia and the CNT deposited on the patch antenna.

Fig. 3 shows the top view of the patch antenna model with a stub placed on the radiating edge to control the resonant frequency. A small gap is placed at the center of the stub where the CNT film is deposited either by ink-jet printing or spray coating. The antenna was designed for 6 GHz operation and printed on photographic paper, about 16 mils (0.4 mm) thick using the Dimatix Printer (www.dimatix.com) shown in Fig. 4. Inkjet-printing is a direct-write technology by which the design pattern is transferred directly to the substrate, and

there is no requirement of masks contrary to widely used photoetching techniques. This aspect, together with the fact that the chemicals necessary for etching are eliminated, makes this approach environmentally friendly as well being of a low cost.

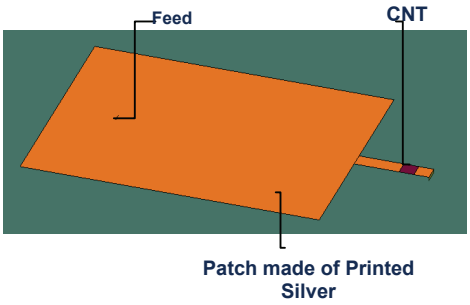
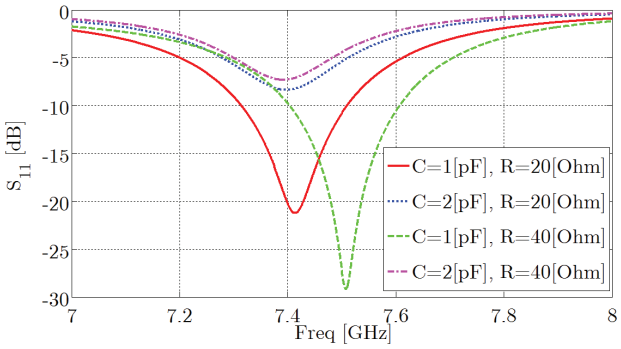


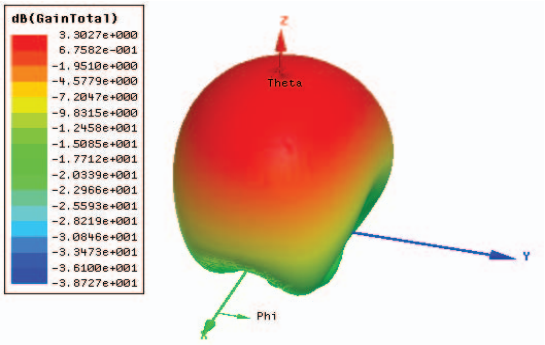
Fig. 3. Sketch of the patch antenna with CNT loading.

Fig. 4. Dimatix ink-jet printer used to fabricate the antenna.

The CNT, essentially a lossy surface coating, affects the efficiency of the antenna. However, its chemical reaction with ammonia or other analyte of interest to which the CNT is functionalized, changes its the effective permittivity, thereby shifting the resonant frequency. There has been previous work published on gas sensors, wherein the resonator is completely coated with the CNT [1], [2], and therefore, the losses in the antenna were considerably high, limiting the radiation efficiency and precluding wireless operation. One can minimize the loss by aligning all single-walled CNT's in the direction of the electric field in the substrate [10], a cumbersome and expensive operation. CNTs are highly conductive only in the form of a single tube or a bunch of tubes with aligned domains. With a mesh of randomly oriented CNTs, the conductivity is reduced considerably. In this paper, with the goal of low-cost ink-jet printing in mind, we prepare a solution of CNT's for depositing on the paper substrate, producing a mesh of randomly oriented CNTs. To minimize the loss resulting from lower conductivity with such a matrix, we separate the antenna and the sensor locations, as shown in Fig. 3. We coat only a small portion of the antenna stub (not the radiator) with CNTs, and the rest, including the patch, is fabricated using deposition of highly conductive silver nano-particles. By doing so, the entire radiator is made of silver, and only a very small portion of the sensor consists of CNTs. Thus, the efficiency of the antenna remains high, and the frequency shift of the return loss is maximized by the change in impedance of the CNT load upon interaction with ammonia.



(a)



(b)

Fig. 5. Simulated results of printed patch antenna with loaded CNT. (a) Return loss corresponding to change in impedance (b) 3-D far field radiation pattern.

Based on the measured CNT surface impedance (Sec. II), we have modeled the CNT as a lumped load comprising a resistance and a capacitance in parallel. We implemented a patch antenna on paper substrate using this load termination in HFSS, and simulated the return loss and radiation pattern. Fig. 5(a) shows a sample design based on the probe-fed patch antenna layout shown in Fig. 3, outlining how the change in CNT impedance affects the return loss. The increase in resistance shifts the return loss to higher frequencies, whereas the increase in capacitance reduces the return loss. By using only a small portion of the antenna as CNT, it is still possible to maintain an acceptable gain of 3.3dBi, according to pattern depicted in Fig. 5(b).

IV. FABRICATION

The sensor fabrication involved several steps. The inset patch antenna designed was inkjet printed onto photo-paper, chosen for hydrophobic nature of its coated surface. Silver nano-particles were used to make low-cost antennas for mm-Wave sensing applications using inkjet printing of silver nano-particles on paper substrates as well as liquid crystal polymers [3-7]. The conductive silver ink jetted precisely through the nozzles of the printer produces the desired metallization pattern. Note that silver has conductivity about 10 times greater than copper in bulk form.

PABS-SWNT, a water-soluble nanotube–polymer compound formed by covalently bonding the polymer, poly(m-

aminobenzene sulfonic acid) (PABS), to SWNTs via amide functionalization [11], were obtained from Carbon Solutions. (www.carbonsolution.com). The functionalized PABS-SWNTs were 1.1µm in diameter and 0.5-1µm in length.

Chemical functionalization is a method to enhance both processibility and sensing performance of SWNTs. First, it allows the unique properties of SWNTs to be coupled to other materials, such as conducting polymers, metals and metal oxides, to create hybrid sensing materials with enhanced sensitivity, selectivity and faster response time. Second, it can improve dissolution and dispersion of SWNTs in various solvents, including water, which enables cost-effective methods to fabricate sensors by simple dispensing or printing techniques.

PABS-SWNT solution in water was prepared for printing CNTs on the substrate. In solid form, SWNTs are highly entangled and associated in macroscopic bundles. So, in order to disperse this in water, it requires significant effort to break these bundles and dissolve the material. First, 50 mg of material was sonicated in 2 ml water for 30 min. Then, 8 ml of water was added and sonicated for additional 90 min. Then the dispersion was stayed overnight at room temperature to observe stability in suspension. Finally, the antenna was cured for 8 hours at 120 degrees Celsius. Fig. 6 shows the fabricated sensor with CNT deposited on the stub.

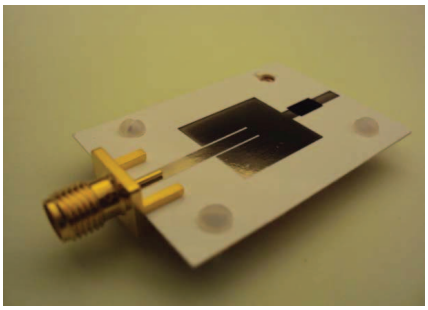


Fig. 6. Fabricated inset patch antenna with loaded PABS-SWNT.

V. Measured Results

Return loss measurements were conducted using an ammonia gas permeation tube in a vacuum hood and a programmable network analyzer. The concentration of ammonia was controlled electronically using the permeation tube and an auxiliary source of nitrogen. The antenna was clamped under the hood, and ammonia, mixed with appropriate quantity of nitrogen, was released over the surface of the sensor. Return loss of the antenna was measured in ambient air under the hood for 3 minutes first to establish baseline. Next, 25 ppm ammonia was released over the sensor for 3 minutes and the return loss was measured at periodic intervals. Finally, the ammonia was mixed with nitrogen to bring the environment back to ambient, and the sensor was examined for 10 min. to check if it would revert back to its nominal condition before exposure.

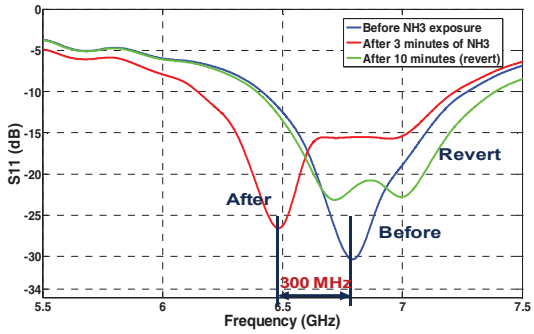


Fig. 7. Measured return loss with ammonia gas showing a resonance frequency shift of 300 MHz when exposed to 25 ppm ammonia.

Fig. 7 shows the return loss for the three states and clearly demonstrates a shift of 300 MHz in resonance when exposed to 25 ppm ammonia. After bringing the environment back to ambient, the sensor reverted back close to the original resonance at 6.8 GHz.

VI. Conclusion

A patch antenna topology has been modified in order to be used as an ammonia gas sensor using functionalized PABS-SWNT as the sensing agent and inkjet-printing implementation. This sensor has demonstrated a maximum sensitivity of 300 MHz resonance frequency shift at 6.8 GHz operating frequency. This shift is the highest reported by 1-2 orders of magnitude with respect to previous attempts. This inkjet-printed gas sensor can be easily integrated with RFID chips for potential low-cost "smart skin" applications in remote chemical and biological sensing.

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