Passive Ammonia Sensor: RFID Tag Integrating Carbon Nanotubes

C. Occhiuzzi [(1)], A.Rida[(2)], G. Marrocco[(3)] , M. M. Tentzeris[(4)]

[(1)]occhiuzzi@disp.uniroma2.it
[(2)]arida@gatech.edu
[(3)]marrocco@disp.uniroma2.it
[(4)]emmanouil.tentzeris@ece.gatech.edu

***Abstract*—In this paper Single-Wall Carbon Nanotubes (CNT) are examined for the design of a passive RFID sensor. CNT film, the so called "buckypaper", is produced and indirectly characterized from a dielectric and a sensititvity point of view. A CNT-based RFID tag prototype is then described as the featured maintenance free sensor and experimentally verified for its applicability and sensitivity towards NH_3.**

I. Introduction

There has been increasing effort in last years towards combining the capabilities of sensors and wireless devices in order to sense, process and transmit information about objects/personnel. Radio Frequency Identification (RFID) passive sensing has been successfully explored as a low cost candidate towards lightweight, reliable, energy efficient and even battery-less durable wireless sensing devices. In addition to RFID's basic identification capabilities, the integration of sensors finds existing and novel applications such as temperature sensing, smart skin applications or structural health monitoring, bio-sensing, and gas sensing [1].

One of the most attracting application is the remote monitoring of environments such as sensing the air for the presence of hazardous gases in industrial environments like supply chain and food monitoring or for monitoring the quality of work area of workers. Traditional gas sensing mechanisms exploit semi-conducting oxides as sensitive material which require micro-fabrication techniques, power supply and specific electronics. Carbon Nanotubes (CNT) composites [2] have been recently found to perform as a gas sensor since their electrical conductance is highly sensitive to small quantities of ammonia (NH_3) and other gaseous [3]. It is not surprising either that CNT and other nanoscale devices are being thoroughly studied for a wide range of applications for high frequency electronics including chemical sensors, field effect transistors, and nano-electromechanical systems [4]. Several CNT based antennas have also been developed for their attractive characteristics [5], [6], [7], however no attempt for using them as a sensor was taken.

In this work, the integration of single wall carbon nanotubes (SWCNT) with a conventional passive RFID antenna is demonstrated for the first time as a battery-less wireless ammonia sensor. The physical rationale of the proposed sensor, lies in the clear dependence of the tag's radiation performances on the physical and chemical features of the integrated CNT, which is strongly affected by the close surrounding environment. When the environment where the tag is placed undergoes changes along with time (ammonia or other gases are present), the CNT's electrical features (conductivity σ) accordingly change affecting the tag's performance, and these variations can be remotely detected by the reader.

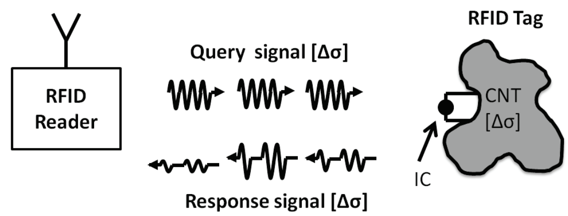

Figure 1. The change of the electromagentic response of CNT-based RFID tag can be related to a variation of the environment surrounding it.

The SWCNT, after their formation in thin film, *buckypaper*, have been characterized at RF. Then an RFID passive tag was designed and matched to a commercial RFID IC. The feasibility of passive RFID tag acting as sensor is here theoretically and experimentally fully investigated in the American and European UHF band.

II. SWCNT Material Preparation and Characterization

Several deposition techniques have been proposed for CNT-based antenna and electronics: inkjet and screen-printing procedures [8], CVD processes [7] and thin films [6] are recent examples of useful techniques able to offer high conductive CNT samples.

SWCNT film, also referred to as *buckypaper*, can be made by filtering SWCNT dispersion in aqueous or organic media, such as Triton X-100 or dimethyl formamide (DMF), under positive or negative pressure. It offers isotropic conductivity, good mechanical strength and flexibility and moreover the film gives the possibility to easily cut out the shape of the desired antenna [9].

In this work an alternative preparation method is presented, where the filtration over membrane has been replaced by evaporation in a controlled environment. The process is schematically shown in Fig.2(left). A 100 mg purified, high functionality with carbonaceous purity $\geq 90\%$ SWCNT powder from Carbon Solutions, Inc has been dispersed in 66mL of water by sonication at 30W for 60 min. Next, in order to get rid of the water and form the CNT bucky paper, an overnight evaporation of the water at 70ºC took place. Finally a circular sheet with $r = 90mm$ and predicted thickness $t = 32\mu m$ has been produced over a polyamide membrane. The thickness of the buckypaper is determined by the total amount of CNTs used in the dispersion per unit surface of the membrane. With a calculated density of $1.6 \times 10^{-2} mg/mm^2$, the thickness is estimated to be $32\mu m$ [10].

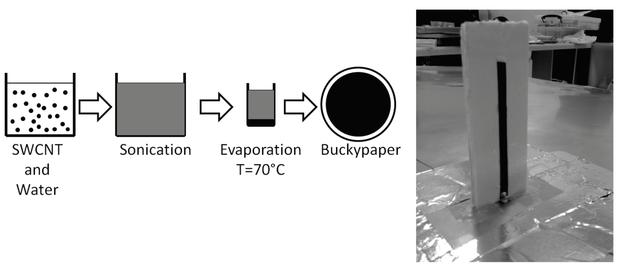

Figure 2. Left) Buckypaper preparation steps. Right) CNT Monopole over ground plane.

The sonication and the evaporation/filtration procedures are extremely important for optimizing the CNT buckypaper performance. It is to be noted that large CNT agglomerates in the CNT solution will dominate leading to a brittle sheet, as well as a non uniform evaporation produces non uniform sheet with holes and consequently non isotropic conductive performances.

The dielectric properties of CNT are strictly dependent on their deposition techniques. Concentration, orientation, number of layers and material type are important parameters that effect the performances of the nanotubes, especially at RF. Although several characterization have been proposed, especially in DC, the dielectric properties are not univocally defined, making necessary to preliminarily produce an RF characterization of the specific produced buckypaper. Here, an indirect characterization method has been used to refine the different values available in literature according to our specific sample. Based on the assumption that CNT is considered as a lossy metal (with finite conductivity σ), several types of monopole-antennas considering CNT buckypaper as conductive element have been designed, simulated and measured by means of a Vector Network Analyzer (VNA Rohde&Schwarz ZVA8). An r.m.s. minimization has been applied in order to fit the measured and simulated input impedances and thus estimate the conductivity. For each run, the best minimizing σ has been considered. After averaging the different results the conductivity of buckypaper has been evaluated as $\sim 2.5 S/m$.

A. Sensing Characterization

The response of the CNT to the ammonia is here investigated.

According to the previous analysis, a strip of the CNT buckypaper of dimensions $80mm \times 5mm$ was cut out of the membrane and plated on a foam substrate in order to form a monopole antenna in the RFID UHF frequency band. Fig. 2 (right) shows the photograph of the monopole antenna as was used in the measurement setup. A silver epoxy mixture was applied at the interface CNT antenna - SMA connector and cured for their conductive and mechanical connectivity. Fig.3 (thick line) shows the measured Z_{in} of the monopole CNT antenna without NH_3. As shown, due to the high losses, the monopole is strongly capacitive with a $-110 \leq jX_{in} \leq -70$ Ohms and with a resistance $30 \leq R_{in} \leq 80$ Ohms.

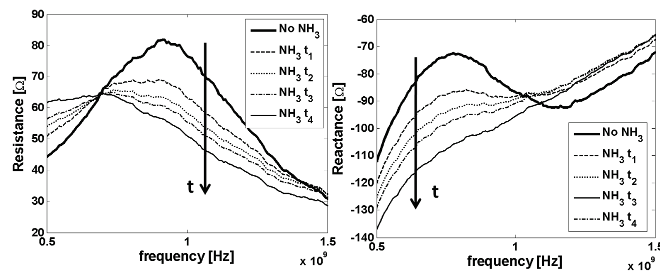

Figure 3. Z_{11} results of the monopole CNT antenna of Fig. 2 with and without the presence of the NH_3.

A volume of $6ml$ of a commercial off the shelf 10% ammonia hydroxide was then guided in a $460cm^3$ plastic chamber surrounding the monopole. Upon the addition of the ammonia, a quick and strong response was recorded. This is shown in Fig. 3 where t_1 indicates the time the measurements were recorded right after the introduction of ammonia. A monotone effect is also observed on R_{in} and X_{in} as time progresses. Here $t_4 - t_1 \approx 15min$. Slight saturation in the recorded measurements are observed as well.

While the exact concentration of ammonia (ppm), is unknown, the proof of concept of using CNT antenna as a chemical sensor is demonstrated.

III. RFID Gas Sensor: design and prototype

There are several options to achieve a gas-sensitive RFID tag taking advantage of the sensing feature of the CNT. A first classification could be done considering the CNT as a part of the antenna radiating structure, e.g. an antenna totally or partially made of nanotubes, or considering the buckypaper as a "parasitic" component of the tag, e.g. a variable load placed in close proximity of the radiating structure. Both solutions offer advantages and drawbacks, the best trade off between communication and sensing must be analyzed. Considering CNT as a radiating element it is possible to increase the sensitivity of the device, however lowering the antenna efficiency and the activation distance. These two parameters, together with the cost, are essential in RFID systems. The other solution, on the contrary, offers better communication and cost performances but could suffer of weak gas sensitivity.

In this work CNT is used as a impedance loading on a conventional RFID passive tag. The design choice was a dipole with an inductively coupled loop [12], matched to an NXP TSSOP8 RFID IC with complex impedance Z_{IC}= 16-j148 Ohms. In this design (Fig. 4), the strength of the coupling is controlled by the distance between the loop and the radiating body, as well as by the shape factor of the loop. A rectangular piece of CNT buckypaper, whose conductivity σ in absence of ammonia has been considered equal to 2.5 S/m according to the previous analysis, was then placed in the space between the loop and the radiating body. The dimension of the RFID Antenna with the CNT loading are shown in Table I.

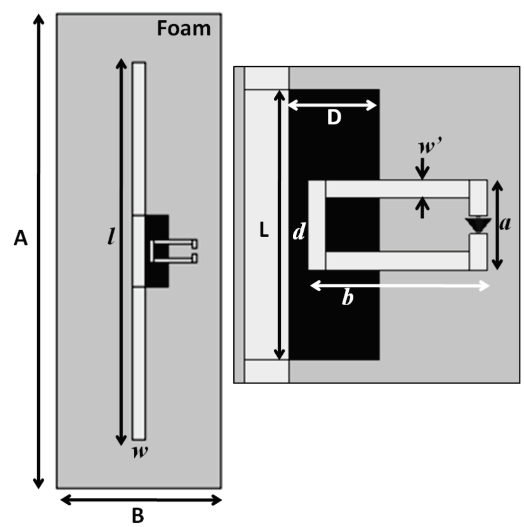

Figure 4. RFID Tag: Dipole with inductively Coupled Loop loaded by a rectangular CNT layer (in black).

Table I
RFID ANTENNA DIMENSIONS

Parameter	Dimension [mm]
A	180
B	80
l	160
w	5
L	30
w'	2
a	10
b	22
d	2
D	10

For the measurements, a Voyantic Tagformance was used with a Kushcraft antenna having a 6dBi gain and a circular polarization. The reader-tag distance is fixed to $63.5cm$. Both the reader and the tag are $101cm$ high from the floor. All the measurements have been conducted into the anechoic chamber.

A performance parameter of the tag to be considered here is the *realized gain* G_τ, e.g. the gain of the tag scaled by the mismatch to the IC. It can be derived from Friis transmission equation, considering the IC sensitivity P_{chip}:

$$G_\tau = (\frac{4\pi d}{\lambda_o})^2 \frac{P_{chip}}{G_R(\theta_R, \phi_R) P^{to} \eta_p} \quad (1)$$

where d is the reader-tag distance, λ_o is the freespace wavelength, $G_R(\theta, \phi)$ is the gain of the reader antenna, P^{to} is the power entering the reader's antenna that is required to activate the tag, η_p is the polarization mismatch between the reader and the tag. P_{chip} is here $-15dBm$. Measured and simulated G_τ are compared in Fig. 5. Although there are some deviations at the lower and higher frequencies, they fit very well around the designed frequency of 915MHz , demontrating the reasonableness of the assumptions in Sec. II.

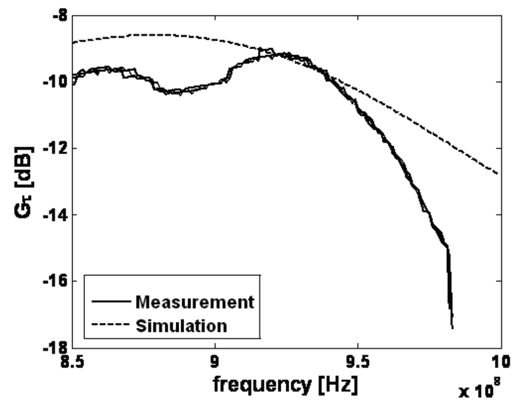

Figure 5. Simulation and Measurement Results for the Realized Gain of the CNT-based RFID Tag.

IV. SENSING CHARACTERIZATION

Using the same setup as before, the sensing performances of the tag have been tested. The tag has been placed into a $684cm^3$ plastic gas chamber, and a volume of $6ml$ of a commercial off the shelf 10% ammonia hydroxide was guided into it. The reference condition for the tag, without ammonia, accounts for the presence of the gas chamber in close proximity of the radiating structures.

Fig. 6 shows the plots of the turn-on P^{to} in dBm for the DUT following the exposition of the tag to NH_3. An immediate and strong response is observed at $t1 = 1min$ followed by a saturated response of P^{to} at $t2 = 4min$, $t3 = 6min$, $t4 = 9min$, and $t5 = 15min$. The behaviour is monoton, with about $2dB$ of overall variation.

Fig.7 shows the recovery plots of P^{to} vs. frequency having removed the ammonia for $t1 = 5min$, $t2 = 13min$, $t3 = 40min$, $t4 = 50min$, and $t6 = 60min$. A monotone recovery characteristic has also been shown here, with a slower response.

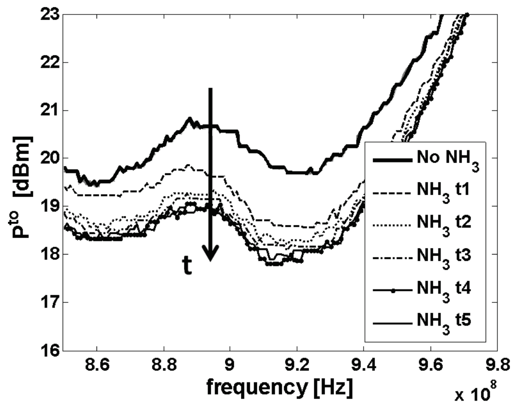

Figure 6. Turn on Power of the CNT loaded RFID Tag with NH_3.

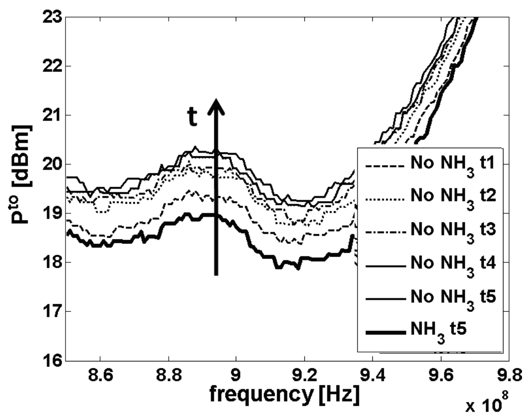

Figure 7. Turn on Power of the CNT loaded RFID Tag - Recovery.

The presence of ammonia irreversibly modifies the tag's radiation performances: a difference of about 10% in the turn-on power is observed between the initial condition (without ammonia) and the final condition (after recovery). As shown in Fig.8 an hysteresis in present all along the process.

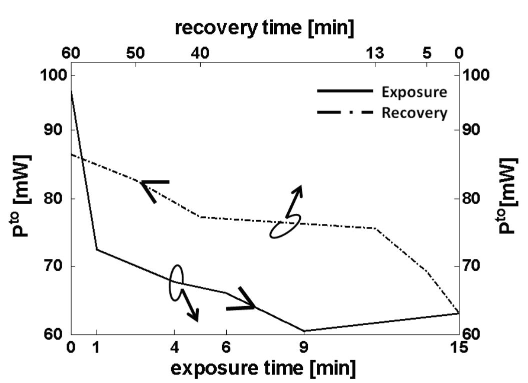

Figure 8. Turn-on power P^{to}at $915MHz$ during the exposure and the recovery process.

V. Conclusions

CNT buckypaper has been realized and indirect methods have been applied for its electromagnetic characterization. Tests show proof of concept of using CNT-antenna as an NH_3 sensor in spite of the strikingly low σ. Finally a novel low cost CNT-based passive RFID Tag was demonstrated for the first time as a maintenance free gas sensor.

The same idea can be implemented in many passive RFID systems and could also serve as a one-shot sensor for perishable foods taking into account the long recovery times and the permanent physical modifications shown. Finally, different functionalizations of the CNT's can lead to different selective multiple-detection RFID sensors for chemo and biodetection.

Improved CNT buckypaper formation and methods aimed to reduce the recovery times, as well as a more quantitative analysis on the sensing capabilities will be shown at the Symposium.

References

[1] G. Marrocco, "Pervasive electromagnetics: sensing paradigms by passive RFID technology", *IEEE Wireless Communications*, Vol. 17, Issue 6, pp. 10 - 17. Dec. 2010

[2] P. Avouris, J. Appenzeller, R. Martel, and S.J. Wind, "Carbon nanotube electronics", Proceedings of the IEEE, vol. 91, issue. 9, pp. 1772-1784, Nov. 2003

[3] S. Chopra, S. Natarajan, and A.M. Rao, "Gas Sensing using Carbon nanotube-based resonator" Proceedings of the IEEE Sensors. pp. 399-402, Vienna, Austria, Oct 2004.

[4] N. Rouhi, D. Jain, and P.J. Burke, "Nanoscale Devices for Large-Scale Applications", *IEEE Microwave Magazine*. vol.11, n.7, pp.72-80, Dec. 2010

[5] P. Russer, N. Fichtner, P. Lugli, W. Porod, J.A. Russer, and H. Yordanov, "Nanoelectronics-Based Integrated Antennas", *IEEE Microwave Magazine*. vol.11, n.7, pp.58-71, Dec. 2010

[6] A. Mehdipour, I. Rosca, A. Sebak, C.W. Trueman, and S.V. Hoa, "Advanced Carbon-Fiber Composite Materials for RFID Tag Antenna Applications" Applied Computational Electromagnetics Society ACES Journal, Special Issue on Computational and Experimental Techniques for RFID Systems and Applications, Part I, pp. 218-229, vol. 25, no. 3, March 2010

[7] Y. Zhou, Y. Bayram, F. Du, L. Dai, and J. Volakis, "Polymer-Carbon Nanotube Sheets for Conformal Load Bearing Antennas" IEEE Transactions on Antennas and Propagation, pp. 2169-2175, vol. 58, no. 7, July 2010

[8] L. Yang, R. Zhang, D. Staiculescu, C.P. Wong, and M.M. Tentzeris, "A Novel Conformal RFID-Enabled Module Utilizing Inkjet-Printed Antennas and Carbon Nanotubes for Gas-Detection Applications" IEEE Antennas and Propagation Letters, vol. 8, pp. 653-656, 2009

[9] M. Meyyappan, Carbon Nanotubes Science and Applications, CRC Press LLc, 2005

[10] A. Mehdipour, I. Rosca, A. Sebak, C. Trueman, and S. Hoa, "Full-Composite Fractal Antenna Using Carbon Nanotubes for Multiband Wireless Applications" IEEE Antennas and Wireless Propagation Letters, pp. 891-894, vol. 9, 2010

[11] K.G. Ong, K. Zeng, and C.A. Grimes, "A Wireless, Passive Carbon Nanotube-Based Gas Sensor" IEEE Sensors Journal, pp. 82-88, vol. 2, no. 2, April 2002

[12] G. Marrocco, "The Art of UHF RFID Antenna Design: Impedance-Matching and Size Reduction Techniques" IEEE Antennas and Propagation Magazine, vol. 50, issue 1, pp. 66-79, Feb 2008

[13] C. Occhiuzzi, and G. Marrocco, "Sensing the Human Body by Implanted Passive RFID Tags" Proceedings of the Fourth European Conference on Antennas and Propagation, pp. 1-5, Barcelona, Spain, 2010