Inkjet-Printed Paper-Based RFID and Nanotechnology-Based Ultrasensitive Sensors: The "Green" Ultimate Solution for an Ever Improving Life Quality and Safety?

Manos Tentzeris and Li Yang

Georgia Electronic Design Center, School of ECE, Georgia Tech, Atlanta, GA 30332-250, U.S.A.
{etentze,liyang}@ece.gatech.edu

Abstract. The paper introduces the integration of conformal paper-based RFID's with a Single Walled Carbon Nanotube (SW-CNT) composite for the development of a chipless RFID-enabled wireless sensor node for toxic gas detection and breathing-gas-content estimation. The electrical performance of the inkjet-printed SWCNT-based ultra-sensitive sensor if reported up to 1GHz. The whole module is realized by inkjet-printing on a low-cost "green" paper-based substrate designed to operate in the European UHF RFID band. The electrical conductivity of the SWCNT film changes in the presence of ultra-small quantities of gases like ammonia and nitrogen dioxide, resulting in the variation of the backscattered power level which can be easily detected by the RFID reader to realize reliable early-warning toxic gas detection or breathing monitoring with potentially profound effects on ubiquitous low-cost "green" quality-of-life applications.

Keywords: Nanotechnology, RFID, carbon nanotube composites, green technologies, gas sensing, conformal/wearable sensors, inkjet printing, wireless sensor, quality-of-life, gas detection, biomonitoring.

1 Introduction

The steadily growing Radio Frequency Identification (RFID) industry requires an ever improving performance of the RFID systems, including reduced size and cost, and higher levels of integration. Also, the tag flexibility is becoming a must for almost all applications, including body area networks for medical systems, tracking for pharmaceutical and food industries, supply chain, space and many more. This demand is further enhanced by the need for lightweight, reliable and durable wireless RFID-enabled sensor nodes [1]. Hence, the two major challenges for such applications are the choice of the material and the advanced integration capabilities. The choice of paper as the substrate material presents multiple advantages and has established paper as one of the most promising materials for UHF RFID applications: it is widely available, and the high demand and the mass "reel-to-reel" production make it the cheapest material ever made. Plus, its environmentally friendly features make it extremely

A.B. Sideridis and Ch. Z. Patrikakis (Eds.): e-Democracy 2009, LNICST 26, pp. 55–63, 2010.

suitable for "green" electronic applications. Previous work has demonstrated the successful development of a fully inkjet-printed RFID module on paper [2]. The next challenge is to integrate the sensor on the paper substrate as well. The application of interest for this work is wireless sensing of toxic gas. Carbon Nanotubes (CNT) composites were found to have electrical conductance highly sensitive to extremely small quantities of gases, such as ammonia (NH_3) and nitrogen oxide (NO_x), etc. at room temperatures with a very fast response time [3]. The conductance change can be explained by the charge transfer of reactive gas molecules with semiconducting CNTs [4]. Previous efforts have shown the successful utilization of CNT-based sensors employing the change in resistance [5]. However, due to the insufficient molecular network formation among the inkjet-printed CNT particles at micro-scale, instabilities were observed in both the resistance and, especially, the reactance dependence on frequency above several MHz, which limits the CNT application in only DC or LF band [6]. To enable the CNT-enabled sensor to be integrated with RFID antenna at UHF band, a special recipe needs to be developed.

This paper presents, for the first time, a conformal CNT-based RFID-enable sensor node for gas sensing applications, fully printed directly on paper substrate. Specifically, in this study one benchmarking RFID tag was designed for the European UHF RFID band centering at 868 MHz. The printed CNT particles were Single-Walled Carbon Nanotubes (SWCNT) from Carbon Solutions, which were dispersed in dimethylformamide (DMF) solution and sonicated to meet the viscosity requirement for the inkjet printer. The SWCNT composite is printed directly on the same paper as the antenna, for a low cost, flexible, highly integrated module. The impedance of the SWCNT film forms the sensor part. The antenna was printed first, followed by the 25 layers of the dispersed SWCNT as a load with "gas-controlled" value. When 4% consistency ammonia was imported into the gas chamber, the SWCNT impedance changed from 51.6-j6.1Ω to 97.1-j18.8Ω at 868MHz, resulting in a 10.8dBi variation in the backscattered power from the RFID antenna, that can be easily detected by the RFID reader to realize the "real-time" gas detection.

2 Inkjet-Printed SW-CNT

As a direct-write technology, inkjet printing transfers the pattern directly to the substrate. Due to its capability of jetting one single ink droplet in the amount as low as 1 pl, it has widely drawn attention from the industrial world as a more accurate and economic fabrication method than the traditional lithography method.

To enable the SWCNT to be inkjet printed, a SWCNT ink solution was developed as the first step. Two types of SWCNT, namely, P2-SWCNT and P3-SWCNT were tested. P2-SWCNT is developed from purified AP-SWNT by air oxidation and catalyst removing. P3-SWCNT is developed from AP-SWNT purified with nitric acid. Compared with P2-SWCNT, P3-SWCNT has much higher functionality and is easier to disperse in the solvent. In experiments, P2-SWCNT started to aggregate at the concentration lower than 0.1mg/ml, while P3-SWCNT can go up to 0.4mg/ml and still show good dispersion. Therefore, P3-SWCNT was selected for the latter steps.

The sample SWCNT powder was dispersed in DMF, a polar aprotic solvent. The concentration of the ink was 0.4mg/ml. This high concentration helped the nano particle network formation after printing; otherwise there would be instability in the impedance response versus frequency of the SWCNT film due to insufficient network formation, such as a sharp dropping of resistance value after 10 MHz [7]. The diluted solution was purified by sonicated for 12 hours to prevent aggregations of large particle residues. This is important to avoid the nozzle clogging by SWCNT flocculation during the printing process. One Materials Printer was used to eject the SWCNT ink droplet onto a flexible substrate.

Silver electrodes were patterned with the nano-practical ink from Cabot before depositing the SWCNT film, followed by a 140˚C sintering. The electrode finger is 2mm by 10mm with a gap of 0.8mm. Then, the 3mm by 2mm SWCNT film was deposited. The 0.6mm overlapping zone is to ensure the good contact between the SWCNT film and the electrodes. Four devices with 10, 15, 20 and 25 SWCNT layers with an approximate thickness of 0.75um/layer were fabricated to investigate the electrical properties. Fig. 1 shows the fabricated samples.

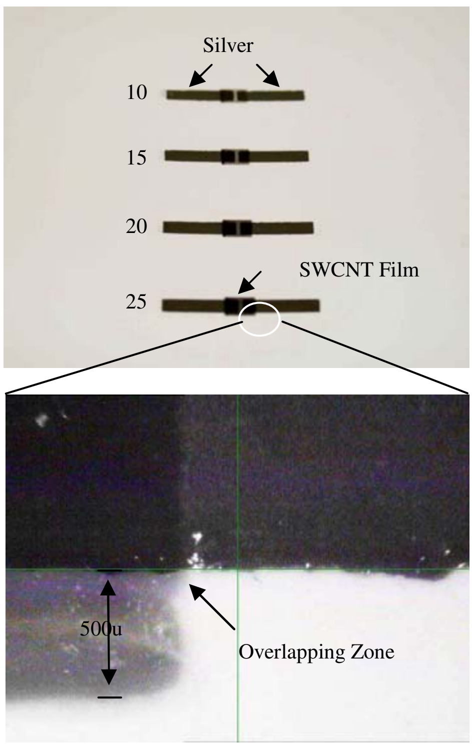


Fig. 1. Photograph of the inkjet-printed SWCNT films with silver electrodes. The SWCNT layers of the samples from up to down are 10, 15, 20 and 25, respectively. The dark region in the magnified picture shows the overlapping zone between the SWCNT and the silver electrodes.

CNT composites have been found to have a very unique resistance performance that can enable the realization of the next generation of sensors with a very high sensitivity up to 1ppb (part per billion), an improvement of 2-3 orders to traditional sensors. The electrical resistance of the fabricated device was measured by probing the end tips of the two electrodes. The DC results in air are shown in Fig. 2. The resistance goes down from when the number of SWCNT layers increases. Since a high number of SWCNT overwritten layers will also help the nano particle network formation, 25-layer film is expected to have the most stable impedance-frequency response and selected for the gas measurement. In the experiment, 4% consistency ammonia was guided into the gas flowing chamber, which includes gas inlet, outlet and exhaust hood. The test setup is shown in Fig. 3. The SWCNT film was kept in the chamber for 30 minutes. A network vector analyzer (Rohde&Schwarz ZVA8) was used to characterize the SWCNT film electrical performance at UHF band before and after the gas flowing. In Fig. 4, the gas sensor of SWCNT composite shows a very stable impedance response up to 1GHz, which verifies the effectiveness of the developed SWCNT solvent recipe. At 868MHz, the sensor exhibits a resistance of 51.6Ω and a reactance of -6.1Ω in air. After meeting ammonia, the resistance was increased to 97.1Ω and reactance was shifted to -18.8Ω.

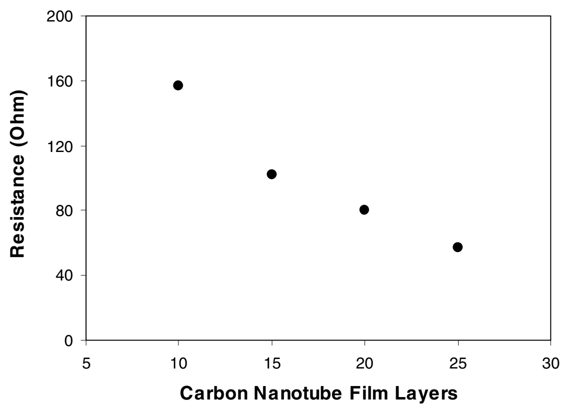


Fig. 2. Measured electrical resistance of SWCNT gas sensor

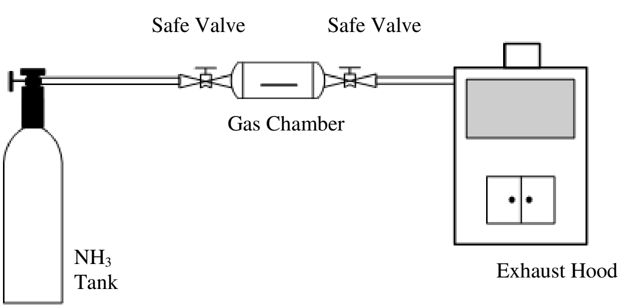


Fig. 3. Schematic of NH_3 gas detection measurement

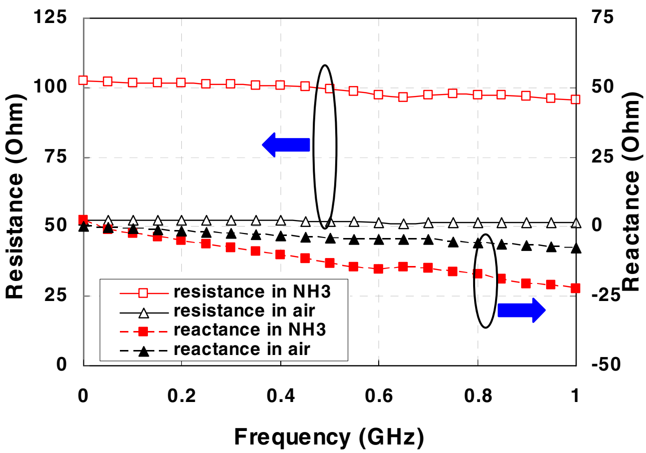


Fig. 4. Measured impedance characteristics of SWCNT film with 25 layers

3 RFID-Enabled "Green" Wireless Sensor Node Module

A passive RFID system operates in the following way: the RFID reader sends an interrogating RF signal to the RFID tag consisting of an antenna and an IC chip as a load. The IC responds to the reader by varying its input impedance, thus modulating the backscattered signal. The modulation scheme often used in RFID applications is amplitude shift keying (ASK) in which the IC impedance switches between the matched state and the mismatched state [8]. The power reflection coefficient of the RFID antenna can be calculated as a measure to evaluate the reflected wave strength.

$$\eta = \left| \frac{Z_{load} - Z_{ANT}{}^{*}}{Z_{load} + Z_{ANT}} \right|^2 \tag{1}$$

where Z_{Load} represents the impedance of the load and Z_{ANT} represents the impedance of the antenna terminals with $Z_{ANT}{}^{*}$ being its complex conjugate. The same mechanism can be used to realize sensor-enabled RFIDs. The inkjet-printed SWCNT film functions as a tunable resistor Z_{Load} with a value determined by the existence of the target gas. The RFID reader monitors the backscattered power level. When the power level changes, it means that there is variation in the load resistance, therefore the sensor detects the existence of the gas, as illustrated in Fig. 5.

The expected power levels of the received signal at the load of the RFID antenna can be calculated using Friis free-space formula, as

$$P_{tag} = P_t G_t G_r \left(\frac{\lambda}{4\pi d} \right)^2 \tag{2}$$

where P_t is the power fed into the reader antenna, G_t and G_r is the gain of the reader antenna and tag antenna, respectively, and d is the distance between the reader and the tag.

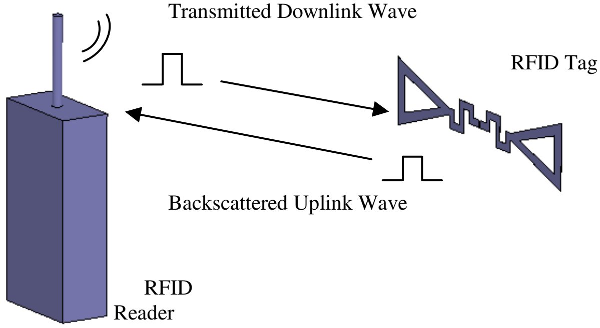
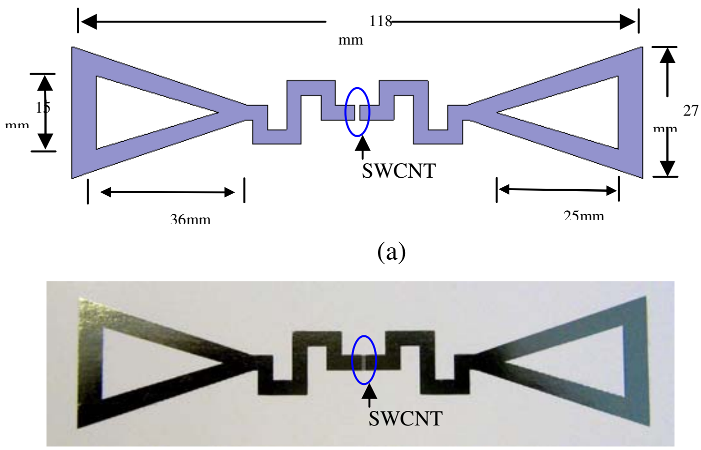


Fig. 5. Conceptual diagram of the proposed RFID-enable sensor



(b)

Fig. 6. The RFID tag module design on flexible substrate: (a) configuration (b) photograph of the tag with inkjet-printed SWCNT film as a load in the middle

Due to the mismatch between the SWCNT sensor and tag antenna, a portion of the received power would be reflected back, as

$$P_{ref} = P_{tag}\eta \quad (3)$$

where η is the power reflection coefficient in (1). Hence the backscattered power received by the RFID reader is defined as

$$P_r = P_{ref} G_t G_r \eta \left(\frac{\lambda}{4\pi d} \right)^2 = P_t G_t^2 G_r^2 \eta \left(\frac{\lambda}{4\pi d} \right)^4 \quad (4)$$

or written in a decibel form, as

$$P_r = P_t + 2G_t + 2G_r - 40\log_{10}\left(\frac{4\pi}{\lambda}\right) - 40\log_{10}(d) + \eta \tag{5}$$

where except the term of η, all the other values remain constant before and after the RFID tag meets gas. Therefore the variation of the backscattered power level solely depends on η, which is determined by the impedance of the SWCNT film.

A bow-tie meander line dipole antenna was designed and fabricated on a 100um thickness flexible paper substrate with dielectric constant 3.2. The RFID prototype structure is shown in Fig. 6 along with dimensions, with the SWCNT film inkjet printed in the center. The nature of the bow-tie shape offers a more broadband operation for the dipole antenna.

A GS 1000μm pitch probe and a dielectric probe station were used for the impedance measurements. The calibration method used was short-open-load-thru (SOLT). The measured Z_{ANT} at 868MHz is 42.6+j11.4Ω. The simulation and measurement results of the return loss of the proposed antenna are shown in Fig. 7, showing a good agreement. The tag bandwidth extends from 810MHz to 890MHz, covering the whole European RFID band. It has to be noted that the flexible property of the paper substrate enables the RFID-enabled module's application in diverse areas, such as in the applications of wireless health monitoring and wearable sensing electronics. In order to verify the performance of the conformal antenna, measurements were performed as well by sticking the same tag on a 75mm radius foam cylinder. As shown in Fig. 7, there is almost no frequency shifting observed, with a bandwidth extending from 814MHz to 891MHz. Overall a good performance is still remained with the interested band covered. Fig. 8 shows the photograph of the designed conformal tag. The radiation pattern is plotted in Fig. 9, which is almost omnidirectional at 868MHz with directivity around 2.01dBi and 94.2% radiation efficiency.

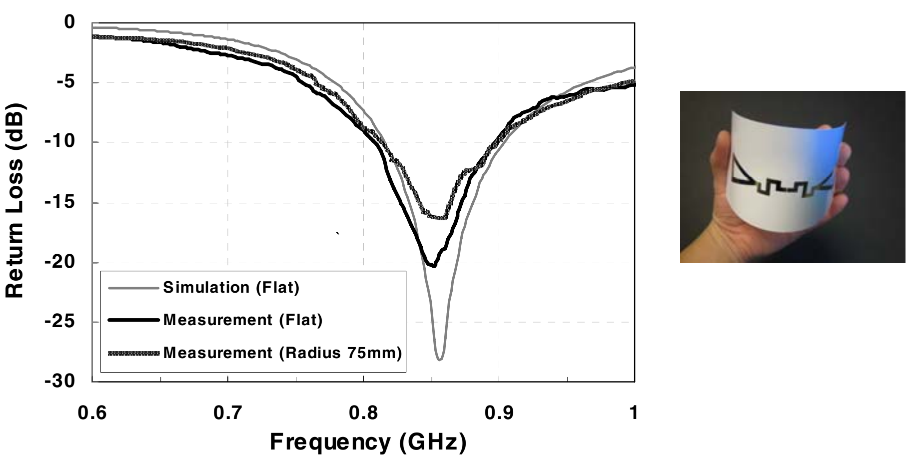


Fig. 7. Simulated and measured return loss of the RFID tag antenna

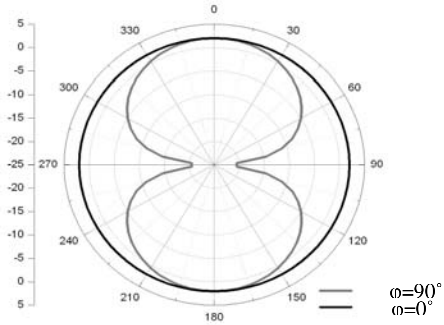


Fig. 8. Far-field radiation pattern plots

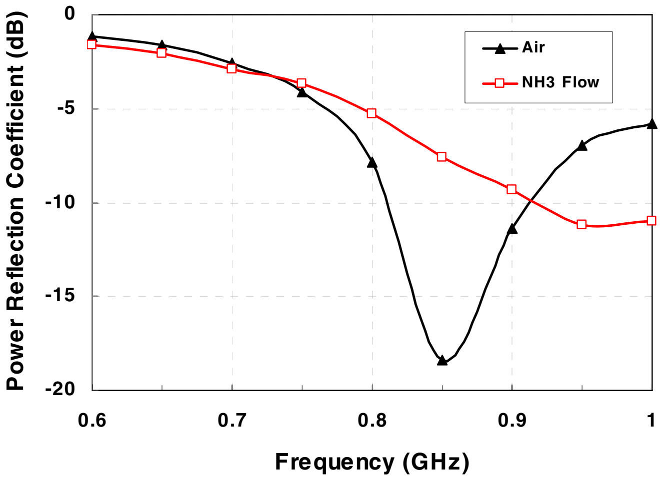


Fig. 9. The power reflection coefficient of the RFID tag antenna with a SWCNT film before and after the gas flow

In the air, the SWCNT film exhibited an impedance of 51.6-j6.1Ω, which results in a low power reflection at -18.4dB. When NH_3 is present, SWCNT film's impedance was shifted to 97.1-j18.8Ω. The mismatch at the antenna port increased the power reflection to -7.6dB. From (5), there would be 10.8dBi increase at the received backscattered power level, as shown in Fig. 9. By detecting this backscattered signal difference on the reader's side, the sensing function can be fulfilled.

4 Conclusions

The inkjet printing method has been utilized to deposit SWCNT film on a fully-printed UHF RFID module on paper to form a "green" flexible ultra-low-cost wireless gas sensor node. To ensure reliable printing, an SWCNT ink solution has been developed. The resistance of the SWCNT film was also characterized up to 1GHz for the first time. The design demonstrated the great applicability of inkjet-printed CNT for the realization of ultrasensitive, fully-integrated “green” wireless RFID-enabled flexible sensor nodes based on the ultrasensitive variabiliity of the resistive properties of the CNT materials with numerous applications in quality-of-life, structural health monitoring, industrial safety and patients’ status biomonitoring.

References

[1] Mishima, T., Abe, N., Tanaka, K., Taki, H.: Toward construction of a mobile system with long-range RFID sensors. In: IEEE conference on Cybernetics and Intelligent Systems, vol. 2, pp. 960–965 (2004)

[2] Yang, L., Rida, A., Vyas, R., Tentzeris, M.M.: RFID tag and RF structures on a paper substrate using inkjet-printing technology. IEEE Transaction on Microwave Theory and Techniques 55, 2894–2901 (2007)

[3] Ong, K.G., Zeng, K., Grimes, C.A.: A wireless, passive carbon nanotube-based gas sensor. IEEE Sens. Journal 2, 82–88 (2002)

[4] Cantalinia, C., Valentini, L., Lozzic, L., Armentano, I., Kenny, J.M., Lozzi, L., Santucci, S.: Carbon nanotubes as new materials for gas sensing applications. J. Eur. Ceram. Soc. 24, 1405–1408 (2004)

[5] Yun, J.-H., Chang-Soo, H., Kim, J., Song, J.-W., Shin, D.-H., Park, Y.-G.: Fabrication of Carbon Nanotube Sensor Device by Inkjet Printing. In: 2008 Proc. of IEEE Nano/Micro Engineered and Molecular Systems, January 2008, pp. 506–509 (2008)

[6] Song, J., Kim, J., Yoon, Y., Choi, B., Kim, J., Han, C.: Inkjet printing of singe-walled carbon nanotubes and electrical characterization of the line pattern. Nanotechnology 19 (2008)

[7] Dragoman, M., Flahaut, E., Dragoman, D., Ahmad, M., Plana, R.: Writing electronic devices on paper with carbon nanotube ink (January 2009), ArXiv-0901.0362

[8] Nikitin, P.V., Rao, K.V.S.: Performance limitations of passive UHF RFID systems. In: IEEE Symposium on Antennas and Propagation 2006, July 2006, pp. 1011–1014 (2006)