A Novel Graphene-Based Inkjet-Printed WISP-Enabled Wireless Gas Sensor

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Abstract— **In this paper we demonstrate the design and development of a low-cost, self-powered, wireless sensor solution based on the WISP platform and utilizing thin films produced from environmentally friendly, water-based, inkjet printed graphene oxide (GO) ink. The sensor demonstrates good response to ammonia gas (NH_3), yielding a 6% normalized resistance change within 15 minutes after exposure to a concentration of 500 ppm. In addition, excellent recovery time is achieved using the graphene thin films, with over 30% of material recovery observed within 5 minutes without exposure to high temperature or any UV treatments. In addition to reporting the first ever integration of inkjet-printed water soluble GO inks into low cost RF electronics fabricated on flexible substrates, we also bring gas sensing capabilities to RFID tags relying on purely wireless digital transmission of the sensed information. The introduction of mass producible, stable, environmentally friendly, inkjet printable GO on organic paper/Kapton substrates lays the foundation for the development of a wide range of new low-cost, high performance graphene-based devices, such as inkjet-printed diodes, capacitors and transistors.**

Keywords- Gas sensing, graphene, inkjet printing, RFID, WISP.

I. INTRODUCTION

The fast and reliable detection of poisonous gases is an essential capability for both personal and environmental safety and, as a result, extremely useful to both public interest and industry. Recent advances in sensor technology employ the use of novel nano-materials, such as carbon nanotube (CNT) and graphene, in chemical sensing applications. These materials alter their properties in the presence of a given substance due to their ability to absorb certain compounds. Chemical absorption produces changes in material properties such as real and imaginary impedance, DC resistance, conductance, and effective dielectric constant. These changes can be exploited and monitored to determine the presence of various chemical compounds by translating the material effects into measurable electrical quantities [1].

All related obstacles to design have been overcome with the use of environmentally-friendly graphene oxide (GO) ink, which can be well dispersed in water and easily lends itself to direct write methods of deposition on the sensor substrate. Additionally, an ever-popular organic substrate, Kapton, has been chosen to "host" the graphene films. The reduction process, described in the next section, allows GO to be converted to pure graphene, restoring its unique properties. The aforementioned novel graphene-based sensor is interfaced, hardware- and software-wise, to the WISP UHF RFID EPC Gen2 Tags to form a new generation of low-cost, battery-less wireless sensing and communication platforms. As a result, the second major contribution of this paper is the introduction, for the first time, of gas sensing capabilities to RFID tags relying on purely wireless digital transmission of the sensed information.

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II. INKJET PRINTING OF GRAPHENE SENSOR PROTOTYPE

The core of the wireless gas sensor is a prototype board made from graphene deposited onto Kapton substrate. Conductive silver ink is used to create the traces connecting the graphene pad to the external circuitry.

The first step in the sensor development process is the creation of stable inkjet-printable graphene based ink. This was accomplished by first converting the graphene into GO powder. Unlike pristine graphene which has very poor dispersion in common solvents, GO exhibits excellent solubility in water due to the existence of hydrophilic functional groups on the surface [2], rendering it an excellent candidate for development of eco-friendly water-based inks. After deposition, pure graphene was obtained by the reduction of GO, which reverts the conjugated basal plane and restores the electrical properties. The reduction of GO is considered as one of most promising methods for low-cost, high yield and scalable preparation of graphene materials [3].

A. Creation of Graphene Oxide

The GO was produced by chemical oxidation of graphite using Hummers' method, which introduces oxygen-containing functional groups to exfoliate pristine graphite into individual sheets (graphene oxide). Graphite flake was placed into a $NaNO_3$ /concentrated $H2SO_4$ solution in an ice bath. Subsequently, $KMnO_4$ was slowly added to the solution while maintaining the temperature below 20 °C. The mixture was stirred in the ice bath for 2 hours and for another 30 minutes in 35 °C water bath. Next, 70 °C water was added drop-wise into the flask. The heat generated via exothermic reaction raised the solution temperature up to 98 °C. Next, additional 70 °C water was then added, followed by hydrogen peroxide solution to terminate the reaction. The mixture was filtrated and washed with water to remove excess acid and inorganic salts.

The resulting GO was dried overnight at 55 °C to produce the GO powder. To prepare the GO ink, dry GO powder was dispersed in a water/glycerol solution and sonicated to disperse any aggregated particles.

B. Fabrication via Inkjet Printing

A Dimatix Materials Printer (DMP-2800) Series material deposition system was used to print the silver and the GO ink. The fabrication process involved deposition of 10 layers of conductive silver onto the Kapton substrate, followed by 15 to 25 layers of graphene oxide. First, the 10 layers of silver ink were deposited and cured at 120°C for 8 hours. Next, 2 layers of GO were deposited and cured at 80°C for 4 hours to serve as a foundation for further prints. GO was then deposited in 5 layer increments, with curing in between, to ensure the highest consistency between samples. Before printing the Kapton substrate was treated by UV-Ozone to improve the hydrophilicity. The treated Kapton demonstrated better performance during printing, enabling higher resolution prints and more layers to be printed during a given cycle. Figure 1 below illustrates the printing of GO ink. Figure 2 shows the completed sensor elements prior to reduction of the GO pads.

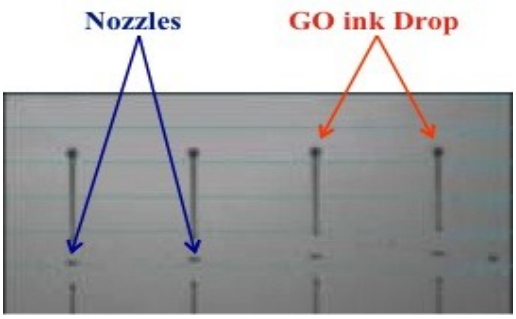

Figure 1. Graphene drop Ejected from inkjet printer.

C. Reduction of Graphene Oxide

Following the printing and curing process, each sample was reduced to obtain the desired graphene. Reduction was achieved by placing the printed GO in a hydrogen and argon atmosphere at elevated temperature for several hours. The reduced graphene oxide layers were characterized via scanning electron microscopy (SEM) to determine their overall quality (i.e. presence of defects in the print, etc.). Figure 3 provides AFM and SEM images of the RGO thin film. Wrinkles on the RGO surface are characteristics of GO/RGO. The examination on the whole patterned area revealed a uniform RGO layer with near 100 % coverage, indicating the high quality of the RGO layer obtained from the ink-jet printing process. AFM imaging revealed an rms average surface roughness of 3.46 nm, with maximum Zmax of 30 nm, further illustrating the film quality.

In addition to thermal techniques, we are also exploring laser reduction as a means to restore the graphene. Although we are in the initial phases of the work, the results appear to be quite promising for enabling graphene based electronics on paper substrate. The temperatures required for thermal reduction can damage paper substrate. However, as shown in Figure 4, we have recently achieved good preliminary results using laser reduction on paper, exposing thin films made from 5 printed layers of graphene oxide to laser delivering 2.35W of continuous power. This power rating is in good agreement with the literature [4]. The result is a thin film exhibiting around 45K Ohm resistance (compared with GO, which is insulator). We believe the high resistance is due to partial discontinuity and incomplete reduction in the film. Further optimization of both film thickness and laser excitation (power, duty cycle, duration, etc) will be necessary to obtain the desired quality of graphene. Most importantly, the laser method will greatly expedite the reduction process and allow selective reduction of the GO thin films to very high accuracy.

Figure 2. Figure 2. Thin graphene films inkjet-printed in between and overlapping silver conductive inkjet-printed trace on Katpon substrate.

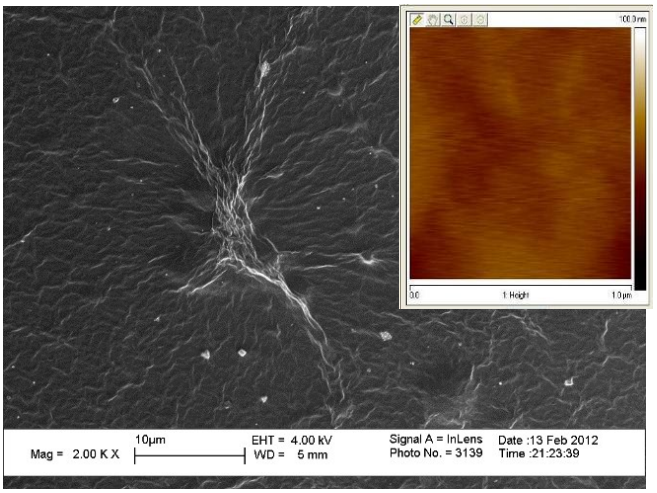

Figure 3. SEM and AFM (inset) images of the RGO thin film.

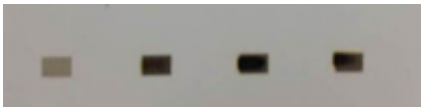

Figure 4. RGO thin films on paper produced via laser reduction techniques.

III. BATTERY-LESS WIRELESS SENSING AND COMMUNICATION PLATFORM

The WISP is a fully passive, battery-free and programmable RFID Tag [5], which can be powered and read by off-the-shelf EPC Gen2 UHF RFID Readers and has an on-board microcontroller for sensing and computing functions. In this work, we modify (hardware- and software-wise) the WISP to create a sensing and communication platform that enables for the first time the introduction of gas sensing capabilities to RFID tags.

As opposed to the distortion-prone analog-based measurement techniques (with the most representative example being the sensing of the shift of the resonant frequency of the antenna sensor), this flexible platform offers the reliability of wireless digital transmission. Our developed prototype WISP-GS (Gas Sensor) platform is shown in Figure 5a. The WISP-GS is solely powered by the RF energy illuminated by a commercial RFID Reader. This 915MHz RF AC current developed across the antenna of the module is rectified and the resulting DC voltage is increased with a charge pump to charge the on-board capacitor. As soon as sufficient energy is accumulated and the voltage across the capacitor monitored by a supervisor exceeds the turn-on voltage of the MCU by an overhead margin, a regulated voltage of 1.805V is used to power both the MCU and our prototype external gas sensing board.

The external WISP-GS board consists, of course, of the graphene-based inkjet-printed RGO sensor, presented in the previous section, as well as the analog interface of this sensor..

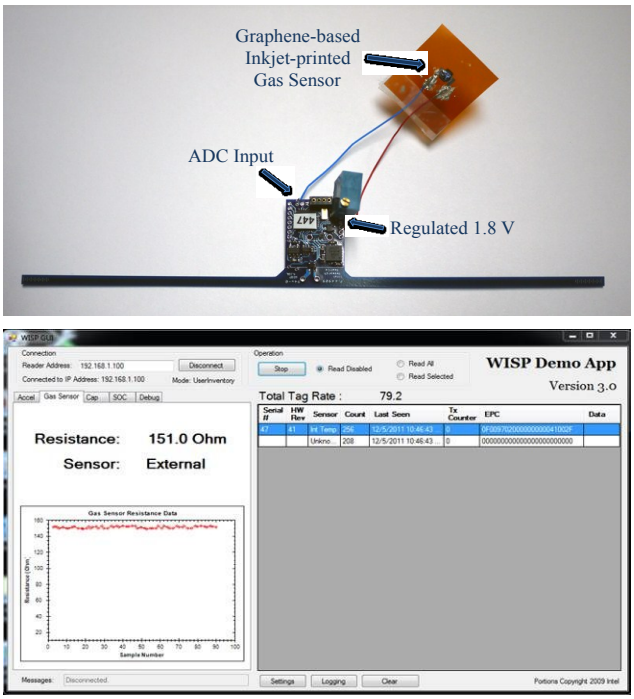

Figure 5. Figure 5. (a) The WISP-GS (Gas Sensor) prototype platform (top). (b) The WISP graphical user interface that captures and plots the sensed information from the transmitted RFID EPC message by the WISP-GS Tag.

For this very first prototype that serves as a proof of concept and because of the small range of the resistance change (6%) relative to the initial resistance, the analog interface is essentially a voltage divider. With this divider the changes in the voltage drop across the gas sensor module, which is directly coupled with the resistance change of the sensor's graphene film pad, can easily be captured with the WISP's integrated Analog-to-Digital Converter (ADC) (pin 2.3). In particular, the impedance of the graphene-based micro-strip line is in parallel with one of the other two in-series resistors of the analog custom board. Of course, special care had to be taken for the selection of the resistors of the voltage divider to not only keep the sensor board's peak consumption less than 2mW but to also maximize the resolution across the whole impedance range that starts from the initial impedance of the graphene-based sensor samples in air and extends to the converged final impedance that corresponds to the application-dependent maximum concentration of the harmful gases under test. Additionally, the typically necessary zero offset has to be set with one-time software code adjustment prior to measurements with each gas sensor. The resolution achieved is equal to the fraction of the maximum resistance value by the 1024 discrete levels of the integrated 10-bit ADC, which yields approximately ± 1 mV accuracy.

Whenever located within the interrogation zone of an RFID reader, the WISP-GS is automatically detected and begins transmission of the sensed information within the EPC message of the RFID communication, as shown in Figure 5b. This figure shows a screenshot of our modified WISP graphical user interface that reports in real time the resistance of the gas film that can be easily mapped to the real gas concentration with the extracted fitting equation, the serial number and type of the sensor, the total number of readings, the time it was last seen as well the full EPC Gen2 message transmitted. The report rate is only a few milliseconds, allowing for immediate reaction to health-threatening gas concentrations.

IV. DESIGN OPTIMIZATION OF THE REDUCED GRAPHENE OXIDE THIN FILMS

Optimization of the RGO thin films was done in order to obtain the proper sensor area to ensure maximum sensitivity. Additionally, it was necessary to obtain the requisite intrinsic impedance of the sensor material to ensure proper operation of the integrated WISP platform. To determine the optimum sensor area, three patterns of differing lengths of RGO material were produced. It was expected that the larger surface area of the last pattern would yield the highest sensitivity. Based on previous efforts in thin film design, it was estimated that between 15-25 layers of the material would be necessary to achieve the desired resistance for the given dimensions of the RGO pads. To validate the assertion, samples of both 15 and 25 layer versions of the patterns were printed and reduced. The measured results can be found in Table 1 below. These represent the average resistance values for a given combination of RGO pad dimension and thickness (# layers).

TABLE 1: AVERAGE INTRINSIC RESISTANCE VALUES OF RGO THIN FILMS.

# LAYERS	PATTERN 1	PATTERN 2	PATTERN 3
15	501.9 Ω	1123.8 Ω	2014.8 Ω
25	248.2 Ω	488.0 Ω	881.8 Ω

V. EXPERIMENTAL SETUP

The sensors were tested using an Environics® S4000 gas mixing system. The setup was capable of producing reliable mixtures up to 500 ppm of ammonia gas diluted in air delivered at a rate of 50 ccm. To calibrate the sensor, the graphene samples were placed into a semi-closed glass chamber to direct the flow of gas onto the sensor. Air flowed

through the system for 15 minutes to establish a system baseline. Next, 500 ppm of ammonia/air mixture was introduced into the system and measurements of the resistance were taken at one minute internals for 15 minutes until near steady state condition in the material was achieved. Finally, the gas source was removed from the device while measurements continued to be taken for another 15 minute interval in order to measure the recovery time.

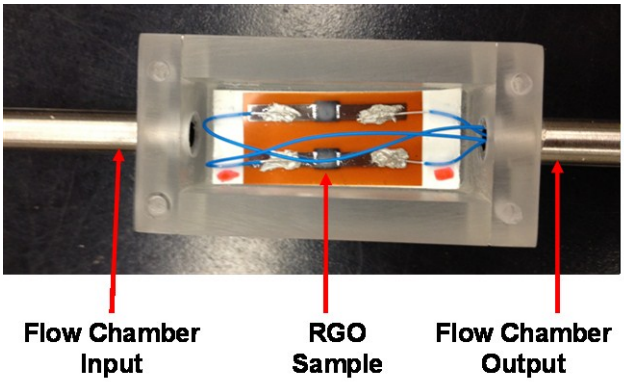

Figure 6. Measurement setup of the graphene sample 2.

VI. Experimntal Results

The results of gas sensing experiments are shown next in Figure 7. The inkjet-printed RGO with different dimensions show similar responses to 500 ppm NH_3. The electrical resistance increases quickly after the introduction of NH_3, indicating a fast detection rate. With the continued supply of NH_3, the resistance change begins to diminish until reaching a saturation region after ~ 10 mins. A maximum sensitivity is observed in the case of Pattern 3, which shows greater than 6 % increase in normalized resistance. The effect of the RGO pattern dimension on the sensor performance is under investigation. Here, it was observed that the pattern with largest area provided the best result. After the introduction of NH_3, pure air was introduced into the system and it was found that the resistance quickly recovered a large portion of its original value (~30%) within 5 mins. The increase in resistance upon the exposure to the gas is due to the electron donation of NH_3 to the p-type RGO film, and is consistent with the literature. Compared to other works on graphene-based gas sensors, our inkjet-printed RGO demonstrates superior performance, including high sensitivity, fast response and quick recovery. Particularly, the short recovery time in natural environmental conditions is hugely advantageous over other reports, which used UV and heat treatment to assist the recovery, and is of great importance for practical applications. The sensor exhibits a 10Ω change in resistance within one minute after introducing NH_3, a measure which is certainly in the detectable range of the backend circuitry of the WISP platform. It is worthy to note here that although the absolute value of the resistance varies between samples, probably due to variances during fabrication, this has negligible influence on the overall performance of the sensor since only the relative changes in resistance are considered here, which are stable between samples.

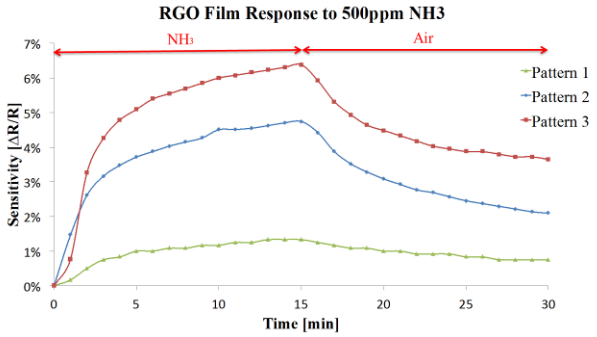

Figure 7. Measured response of RGO thin films in presence of NH_3.

VII. Conclusion

In this work, we have developed a novel self-powered wireless gas sensor based on a WISP platform using reduced graphene oxide (RGO) thin films produced via low cost inkjet-printing methods. Through this endeavor, we introduce for the first time the integration of RF nanotechnology with sensor platforms, leading to ultra-low-cost wireless sensors with unprecedented performance. In addition, we introduce graphene material as a viable useful enhancement to the art of RF electronics. Finally, through our efforts in the development of environmentally friendly, stable, low-cost, inkjet-printable GO inks, we lay the foundation for advancement in high performance inkjet-printed electronics such as inkjet-printed graphene based diodes, super capacitive devices, and transistors. The prototype device exceeded expectations, producing a 6% change in resistance at 500 ppm concentration of ammonia gas. Moreover, the sensor demonstrated fast recovery time in comparison to the current state of technology. These results can be improved upon by optimization of the deposition and curing techniques, and with enhancements to the output circuitry of the final sensor design.

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