Microwatt-Powered, Low-Cost, Printed Graphene Oxide Humidity Sensors for Distributed Network Applications

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Abstract. We report the design, fabrication, and characterization of novel conductometric humidity sensors that employ an ultrathin film of graphene oxide (GO) nanoflakes as transducing element. The GO film is deposited with a shadow mask using an electrospray emitter operated at atmospheric pressure; no post treatments--including annealing or doping--were applied to the GO sensors. The Van der Pauw electrode structure used in the sensor had 50 µm linewidths separated by 600 µm and was fabricated with the lift-off metallization technique. In dynamic humidity tests conducted at atmospheric pressure, the sensor tracks the response of a commercial sensor and reacts to changes in humidity in less than 500 ms. There is a quadratic dependence of the relative humidity on the sensor resistance for the relative humidity range between 3% and 63%, with more than a three-fold change in resistance over the range. The power consumption of the sensor is less than 30 µW while drawing 7 µA, and less than 15 µW while drawing 5 µA. Our devices are promising candidates for deployment in a distributed sensor network due to their low cost, small size, and low power consumption.

1. Introduction

Distributed humidity and temperature sensor networks have been investigated for deployment in commercial buildings as part of energy management of heating, ventilating, and air conditioning (HVAC) systems [1]-[2]. For this application, size, power consumption, reliability, and cost are the main driving metrics for sensor selection. Conductometric gas sensors--based on the chemoresistive response of semiconducting metal oxide films--are widely used due to their simplicity, flexibility in production, and broad applicability to many fields [3]. Typically, the adsorption of a gas molecule on the surface of a metal oxide alters surface electronic properties, causing a change in electrical conductivity [4]. Although many metal oxides could be used for gas sensing, only a few show the appropriate combination of adsorption ability, catalytic activity, sensitivity, and thermodynamic stability. These select metal oxides (e.g., SnO₂, TiO₂, and ZnO), however, are the least active from the catalytic point of view [5]; doping with redox-active noble metal nanoparticles, such as Pt, Au, and Pd, is commonly done to enhance conductivity response and gas sensitivity. Unfortunately, noble metals are expensive, thereby precluding their use in low-cost applications.

An appealing alternative material for reactive gas sensing is graphene oxide (GO) because of its high sensitivity to adsorbed surface species and harsh environment compatibility. Thin-film humidity sensors made of GO, and the related 2D material reduced graphene oxide (rGO), have been deposited in aqueous suspensions by drop-casting and airbrush spraying [6]-[7]. However, electrospray printing
allows for more precise control of the film properties compared with the other techniques and is compatible with low-cost, large-area manufacturing through emitter multiplexing [8]-[11].

In this work, low-cost GO humidity sensors are reported; the devices have a ~60 nm-thick transducing element fabricated at low temperature (< 65 °C) using electrospray printing of nanoflakes with a shadow mask, and no post treatment to the devices was conducted including annealing and doping. Devices with multiple electrode configurations were fabricated on SiO₂-coated Si wafers using contact photolithography and the lift-off technique. Our devices were characterized as humidity sensors using a home-built environmental chamber at atmospheric pressure while varying the relative humidity (RH) between 3% and 63%; the response was benchmarked using a commercial humidity sensor. Electrospray printed rGO thin film structures have recently been reported for humidity detection [12]. However, our electrospray printed GO humidity sensors are superior to those reported in [12] because our GO sensors respond faster, reaching equilibrium more than 30 times quicker at 50 % RH, and because the change of resistance of our sensors has a dynamic range that is an order of magnitude larger.

2. Description of Fabrication Method
The starting substrate is a 1 cm-wide square piece of single-crystal silicon coated with 500 nm of thermal oxide. First, image-reversal contact lithography is conducted in a spun-coated thin film of photoresist to transfer the layouts of the electrodes. Then, a 100 nm Au film on top of a 10 nm Cr film is deposited everywhere on the substrate using the electron beam evaporation technique. After that, the photoresist is dissolved using acetone, which removes the metal stack everywhere on the substrate except at the bottom of the cavities defined by the lithography, leaving behind the electrode pattern. Finally, the GO layer is electrospray printed on top of the electrodes using a home-built apparatus.

The home-built electrospray printer has a syringe pump that delivers an aqueous dispersion of GO nanoflakes to a blunt hollow stainless steel needle with a 300 µm inner diameter. The starting material is a commercial GO solution (Sigma Aldrich product 777676) with a concentration of 4 mg/ml GO in water. We diluted the starting material using deionized water to a concentration of 40 µg/ml. The needle tip is centered in the plane of a grounded stainless steel annular electrode, and a high-voltage power supply biases the needle at around 3kV to produce droplet emission. A shadow mask is placed over the substrate to be printed, which is on top of a hot plate, and the assembly is mounted on a PC-controlled 3-axis stage above the needle. To perform a film deposition, the substrate is first mounted on the heated stage and brought to temperature for about 5 minutes. The GO nanoflake solution is then loaded into the syringe pump, and the system is primed up to the tip of the emitter. After this, the syringe pump is activated, delivering a flow rate around 1 µl/min, and a high bias voltage is applied to the tip and adjusted to yield a stable Taylor cone. The beam of GO droplets is positioned to the side of the substrate and observations are made to ensure that the emission is stable. Finally, a deposition recipe (i.e., a sequence of commands that move the stage in a pre-established fashion) is run.

**Figure 1.** Electrospray printed GO films on a dielectric substrate at different separation distances and stage speeds. The third imprint from the right corresponds to an optimal separation distance of 3 cm.

Optimization experiments with the home-built electrospray printer were conducted to deposit interconnected films by keeping constant the flow rate and bias voltage while varying the separation distance, stage speed, number of passes, and surface temperature. From these experiments, the
optimum separation distance was found to be 3 cm (Figure 1). From the imprints collected, the beam divergence of the electrospray is estimated at 10° semi-angle, which is in agreement with the literature on cone-jet electrospray sources [13]-[14]. Films deposited at temperatures slightly above room temperature (50 – 64°C) were of better quality than those deposited at room temperature; in particular, heated samples had less thickness variation across the coating and did not show the liquid accumulation at the edges of the imprints created on unheated samples.

Originally, a single shadow mask (stainless steel, 250 µm thick, 1.3 mm ID aperture) was used to create the imprints. However, during operation of the electrospray emitter the GO solution wetted the perimeter of the aperture of the shadow mask, and upon drying and mask removal, freestanding walls of GO nanosheets were left on some areas around the edge of the hole, and patches of the imprint were delaminated from the substrate in other areas. To prevent edge sidewall formation and imprint delamination, a two-layer shadow mask was implemented (two stainless steel sheets, each 125 µm thick, bottom layer 1.3 mm aperture, top layer 1.0 mm aperture, concentrically mounted). With the double shadow mask and under optimized conditions, GO films with average thickness <100 nm were successfully manufactured.

Once fabricated, the chips were placed in standard IC packages with Au wire-bonds (Figure 2, left). The sensor has an active area of about 0.4 mm² between the electrodes; the metallization lines underneath the active area are 50 µm wide with 600 µm separation (Figure 2, right). The GO nanoflakes form a connected conductive network between the four electrodes.

3. Characterization of the Devices as Humidity Sensors

The packaged sensors were placed inside a custom-built environmental chamber (Figure 3) where the relative humidity was varied between 3% and 63%. Room air was bubbled through a bottle containing water by pulling a house vacuum on the chamber. The relative humidity in the chamber was varied by mixing the moistened room air with dry nitrogen at the inlet and varying the house vacuum draw at the outlet. We were able to set a maximum RH of about 40 % within the chamber while under flow conditions; we obtained RH levels up to around 60% by isolating the chamber and soaking it for about 20 minutes. A commercial humidity sensor (Honeywell HIH-4000) was mounted near the GO sensor for comparison (Figure 3, right).

In the Van der Pauw electrode configuration of the GO sensor, $I_1$ current was supplied to electrode 1 with a source measuring unit (SMU) Keithley 2612B, electrode 2 was connected to ground, and electrodes 3 and 4 were floating. Voltage readings of the electrodes were logged on the GO sensor and the commercial humidity sensor with a Dataq DI-149, which is an 8-channel data logger and was set to
sample data at a rate of 20 Hz. The resistance across pins 3 and 4 was calculated using the expression 
\[ R_{1243} = \frac{(V_4-V_3)}{I_1} \]
where \( V_4-V_3 \) is the bias voltage between electrodes 4 and 3. Through experimentation of the magnitude of \( I_1 \) it was determined values in the 5-7 µA range yielded the largest difference in voltage between pins 4 and 3.

We conducted two types of experiments to characterize the change of resistance in the sensors with relative humidity: *dynamic response tests* were the humidity was varied quickly while gas was flowing to the chamber, and *static response tests* where the humidity was raised to highest achievable value attainable by the experimental apparatus to then bled down to the lowest value. In both cases, the boxcar averaging technique with a window size of 0.55 s was used to reduce the signal noise. During the dynamic response tests, the resistance change of the GO sensor (red curves of Figures 4(a)-(c)) and the response of the commercial sensor (black curves of Figures 4(a)-(c)) tracked each other closely as the relative humidity was varied rapidly between 10 and 30%. Figure 4(b), which is a magnified view of a rapid humidity transition zone in Figure 4(a), demonstrates that the signal response time is less than 500 ms for the GO sensors and faster than the signal response of the commercial sensor.

**Figure 3.** Home-built environmental test chamber (left) and close-up of GO sensor in the foreground and commercial sensor in the background (right).

**Figure 4.** GO sensor response to dynamically changing humidity ((a)-(c) red curves) compared with a commercially available sensor ((a)-(c) black curves) and RH as a function of the sensor response (d).
Analysis of all the data collected during the experiments evidences a quadratic dependence of the relative humidity on the sensor resistance (Figure 4(d)). The scatter in the data falls within $R_{1243+/-7\%}$ and the HIH-4000 has a sensitivity of $+/-5\%$ RH. In addition, more than a threefold change in the GO printed sensor resistance was measured in the 3-63% RH range. The power consumption of the GO printed sensor is estimated at 30 µW or less over the 3-63% relative humidity range while 7 µA are drawn by the device; if the current drawn by the device is lowered to 5 µA, the power consumption drops to less than 15 µW. The decrease in resistance of the GO sensors with increasing relative humidity found in these experiments followed the same behaviour observed for reported sensors made with drop-cast and airbrush sprayed GO thin films [6],[7].

4. Conclusions
Microwatt-powered conductometric humidity sensors were fabricated by shadow mask electrospray printing at atmospheric pressure and slightly elevated temperatures (< 65°C) of an aqueous suspension of GO nanoflakes onto electrode patterns defined by the lift-off metallization technique. No post treatment was required to activate the devices including annealing or doping with metal nanoparticles. The sensor response to humidity followed that of a commercial sensor and there is a quadratic dependence of the relative humidity on the sensor resistance in the 3-63% RH range studied, with more than a threefold change in resistance over this range. The measured decrease in sensor resistance with increasing RH is in agreement with reported GO sensors fabricated by the drop-cast and airbrush spray methods. Our devices are promising candidates for the humidity sensor on the modules dispersed in distributed sensor networks due to their low cost, small size, and low power consumption.

Acknowledgements
The microfabrication of the devices was completed using the facilities at the Microsystems Technology Laboratories of MIT. This work was supported by Edwards Vacuum.

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