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A low-cost approach to low-power gas sensors based on self-heating effects in large arrays of nanostructures

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Abstract

The usual operation of a conductometric sensor device requires of an external energy source (i.e. an embedded heater). In the last years, the Joule effect in the sensing material, the so called self-heating effect, offered an alternative method to provide this energy: the probing current (or voltage) applied to measure the sensor signal also serves to heat up the sensor active film. Here, evidences of self-heating effects occurring on large arrays of nanostructures fabricated with low-cost methods are provided. The methodology is proven to be suitable to sense gases (humidity, NH₃ and NO₂) with low-powered heater-free devices.

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1. Introduction

Conductometric solid-state gas sensors are a cost-effective solution to monitor the presence of gases. These devices usually operate at high temperatures, typically from 150°C to 500°C, in order to optimize the sensor signal by tuning the chemical processes occurring in the surface of the reactive material. To that reason, the conductometric sensors usually require an external heater component, which is the most power demanding part of the device. The necessity of an auxiliary element (e.g. heater) for sensing increases the fabrication cost and the device power budget (from 100mW

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up to 1W for commercial state of the art devices). Traditionally, attempts to lower the power needs were centered on the fabrication of more efficient heating systems, the use of other energy sources (i.e. low power LEDs) or tuning of the active material properties (i.e. surface functionalization, decoration, the use of hybrid materials) in order to lower the sensor operation temperature. Another approach to solve this issue is harnessing the Joule dissipation occurring at the sensing active material itself [1]. This so-called self-heating effect has been studied in highly ordered nanosized systems (i.e. a single nanowire [2]). This systems involved complex fabrication steps hardly transferable to a higher production scale, hampering the widespread of this methodology in a cost-effective manner. Here, we provide evidences that self-heated modulated response to gases could also occur in large arrays of randomly oriented nanostructures.

In this work, we used carbon nanofibers as active material for the sensors. Carbon materials have gained uprising interest as their electrical, optical and mechanical characteristics make them good candidates for a new generation of low-cost devices [3]. The gas sensing properties of carbon materials have been widely proven, in fact, carbon allotropes show gas response at temperatures below 100 °C or even at room temperature [3].

Here, we show that the probing voltage (or current) used to acquire the electrical signal of a randomly distributed fabric of CNFs can be used to achieve gas responses similar to those obtained with an external heating element (i.e. self-heating). The proposed approach simplifies the use of self-heating dramatically, both in terms of fabrication requirements and operation procedures.

2. Materials & methods

Interdigitated platinum electrodes (IDE) over a ceramic substrate were used. The IDE platform also included an embedded heater and a thermoresistance, this elements were only used for temperature calibration purposes and comparison of gas sensing characteristics between self-heating and the use of an external heater. Large arrangements of carbon nanofibers (CNFs, fig. 1(a)), a carbon allotrope sharing sensing characteristics with carbon nanotubes or graphene, were used as sensing active film. The fibers presented diameters ranging from 30 to 80 nm and lengths up to 75 μm . The CNFs were dispersed in 2-propanol and drop-casted over interdigitated electrodes (fig. 1(b)). Electrical resistance was monitored during the deposition with a digital multimeter Agilent 34401A to assess the continuity of the film.

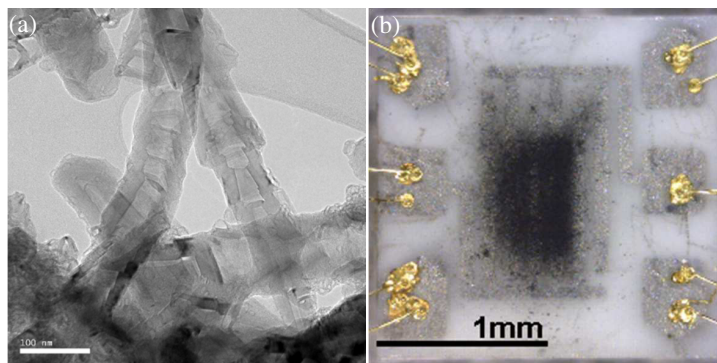


Fig. 1. (a) Transmission electron microscope image of CNFs. (b) Deposition of CNFs over interdigitated electrodes.

Self-heated sensors were operated in atmospheres of N_2 and synthetic air (SA, 21 % in O_2 and 70% in N_2). Gas sensing experiments were conducted in a customized chamber of 20 ml in volume, the gas flow was maintained stable at 200 ml/min during all the measurements. Reference gaseous atmospheres were provided by independent mass flow controllers blending N_2 , SA, NH_3 (100 ppm in SA) and NO_2 (10 ppm in SA). Water vapor was obtained by bubbling dry SA into deionized water. Electrical measurements during gas experiments were performed with a Keithley 2401 source meter.

3. Results & discussion

The sensors were first tested comparing the resistance signal at different temperatures operating the sensor with the external heater and then, using self-heating (fig. 2). For both cases, the CNFs displayed the same semiconductor behavior with temperature. Comparing the resistance levels at different applied probing voltage with its equivalent resistance level using the heater, a temperature vs voltage calibration for self-heating could be extracted. Same behavior was found for N₂ and SA atmospheres.

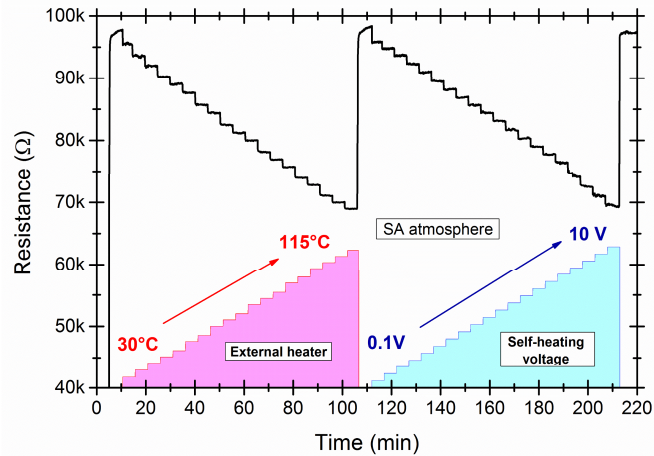


Fig. 2. Transient resistance signal of a CNFs sensor driven by an external heater and self-heating, measurement performed with SA atmosphere. Adapted with permission of the copyright owner.

The response towards humidity was tested as an application for the self-heating methodology. The sensor was exposed to three different concentrations of humidity (100 %, 50 % and 25 %). The gas sensing characteristics were compared heating up the sensor using an embedded heater and by self-heating operation, obtaining similar results for both methods (see fig. 3). Reproduced with permission of the copyright owner.

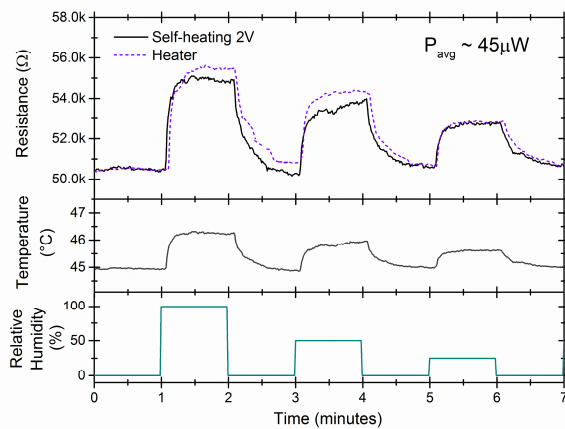


Fig. 3. Comparison of sensor signal obtained by self-heating and by heater operation for a humidity test. Adapted with permission of the copyright owner.

Moreover, self-heating also provides response modulation for other gases such as NO_2 and NH_3 (fig. 4) with a reduction of power consumption from mW to tens of μW .

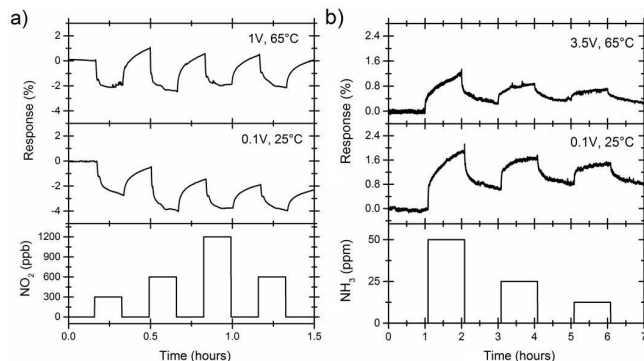


Fig. 4. (a) NO_2 and (b) NH_3 gas sensing response modulation, temperature provided by self-heating. Reproduced with permission of the copyright owner.

The self-heating sensing methodology is shown to be comparable with a heater-driven device with the benefits of the reduction of power consumption and the device complexity. In addition, this approach is not dependent on the sensing material and could be transferable to other gas sensing materials such as metal oxides.

4. Conclusions

It has been demonstrated that self-heating effect occurs in films made of randomly oriented nanoparticles overcoming the complex fabrication requirements of previous attempts and opening the door to the use of this effect in cost effective devices.

Self-heating operation made possible reaching temperatures up to 200°C with power consumption in the range of tens of mW, reaching efficiencies comparable to state of the art micro-heaters with a much simpler approach. For certain low-temperature applications ($<100^\circ\text{C}$) typical power consumptions are in the range of tens of μW .

From the gas sensing perspective, the self-heating methodology is comparable to the use of an external heater. The response to humidity, NH_3 and NO_2 has been modulated using the self-heating effect, open the door to forthcoming free-heater devices.

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References

- [1] J.D. Prades, R. Jimenez-Diaz, F. Hernandez-Ramirez, J. Pan, A. Romano-Rodriguez, S. Mathur, et al., Direct observation of the gas-surface interaction kinetics in nanowires through pulsed self-heating assisted conductometric measurements, *Appl. Phys. Lett.* 95 (2009) 053101. doi:10.1063/1.3192358.
- [2] J.D. Prades, R. Jimenez-Diaz, F. Hernandez-Ramirez, S. Barth, a. Cirera, a. Romano-Rodriguez, et al., Ultralow power consumption gas sensors based on self-heated individual nanowires, *Appl. Phys. Lett.* 93 (2008) 123110. doi:10.1063/1.2988265.
- [3] O. Monereo, J.D. Prades, a. Cirera, Self-heating effects in large arrangements of randomly oriented carbon nanofibers: application to gas sensors, *Sensors Actuators B Chem.* 211 (2015) 489–497. doi:10.1016/j.snb.2015.01.095.