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GRAPHENE SOI CMOS SENSORS FOR DETECTION OF PPB LEVELS OF NO2 IN AIR

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ABSTRACT

There is considerable demand for sensors that are capable of detecting ultra-low concentrations (sub-PPM) of toxic gases in air. Of particular interest are NO_2 and CO that are exhaust products of internal combustion engines. Electrochemical (EC) sensors are widely used to detect these gases and offer the advantages of low power, good selectivity and temporal stability. However, EC sensors are large (~1 cm^3), hand-made and thus expensive (~\$25). Consequently, they are unsuitable for the low-cost automotive market that demands units for less than \$10. One alternative technology is SnO_2 or WO_3 resistive gas sensors that are fabricated in volume today using screen-printed films on alumina substrates and operate at ~400°C. Unfortunately, they suffer from several disadvantages: power consumption is high ~200 mW; reproducibility of the sensing element is poor; and cross-sensitivity is high.

KEYWORDS

Graphene, gas sensor, chemical sensor.

INTRODUCTION

Considerable effort has been directed recently towards the development of low cost, low power micro-hotplates using SOI CMOS technology [1].

Figure 1 shows a schematic of our SOI micro-hotplate. The device comprises a p+-Si heater below interdigitated electrodes (IDEs) onto which a nanoscale gas-sensitive layer is deposited; see Figure 2. The silicon die was fabricated in a 6” wafer SOI CMOS process (XFAB, Germany). The circular SOI membrane is formed using a DRIE back-etch with diameter of 600 μm. The silicon heater has a resistance of 91 Ω at 25°C and diameter of 300 μm. The IDEs have an aspect ratio of 320. The Al electrodes are bump bonded by first Ni and then Au to form an ohmic contact to the sensing layer. The SOI membrane can operate up to 700°C; however, the low Al melting point limits the maximum operating temperature. Key advantages of the designed microhotplates are the very low DC power consumption and the temperature uniformity across the heater sensing area.

Previous work reports the growth of carbon nanotubes (CNTs) on the SOI heaters by CVD at 600ºC [2]. However, the response of the CNTs to low levels of NO_2 was found to be poor [3] and they also suffered from low selectivity.

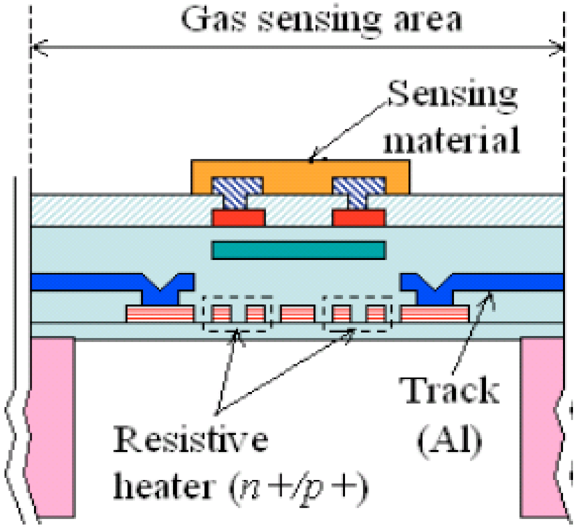

Figure 1: Schematic cross-section of SOI CMOS micro-hotplate with buried doped Si heater and DRIE back-etch to define membrane.

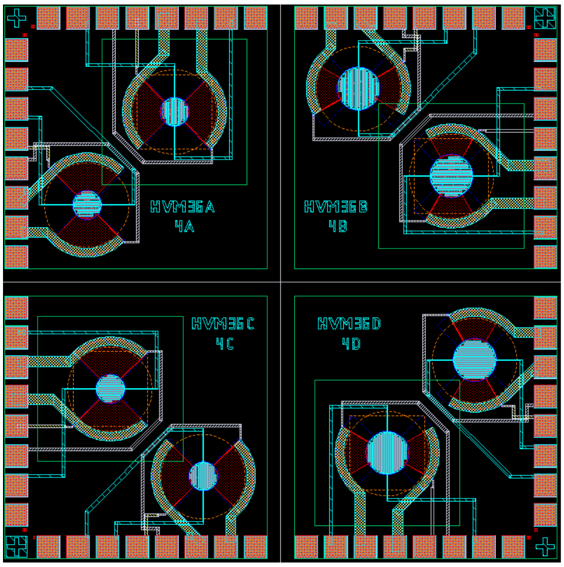

Figure 2: Design of SOI die (3.9mm × 3.9mm) with quadrant 4D diced and used here for testing.

Figure 3 shows an approximately linear relationship between the heater’s working temperature and its power consumption. 37.5 mW of power are dissipated at a temperature of 300 °C, but only 17.5 mW at 150 °C. The

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power dissipation (average) can be reduced considerably further (below 1 mW) when the heaters are driven in a pulsed mode of operation. This driving method is possible because of the very small thermal mass of the SOI membrane, which leads to thermal rise times (10% - 90%) of *ca*. 20 ms.

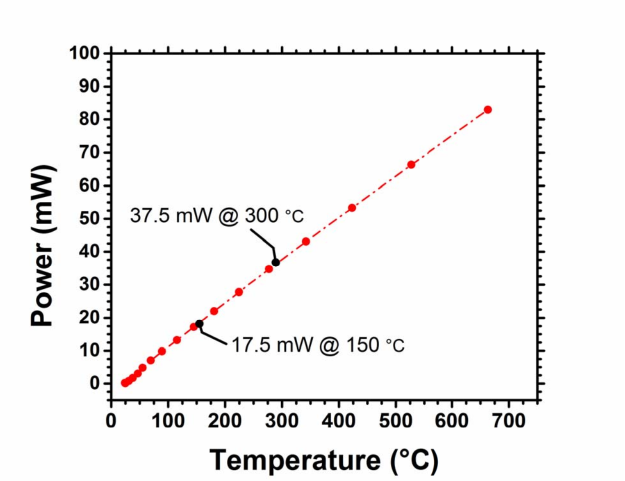

Figure 3: Measured DC power consumption as function of the heater temperature.

Figure 4 shows the simulated temperature distribution across a circular SOI micro-hotplate (from FEM package Ansys). The temperature is highest (as expected) above the heater and decreases almost linearly down to ambient temperature at the edge of the membrane structure. Particular attention has been paid to the geometrical structure of the micro-heater in order to reach an extremely uniform temperature distribution over the entire sensing area (300 ± 8 ºC).

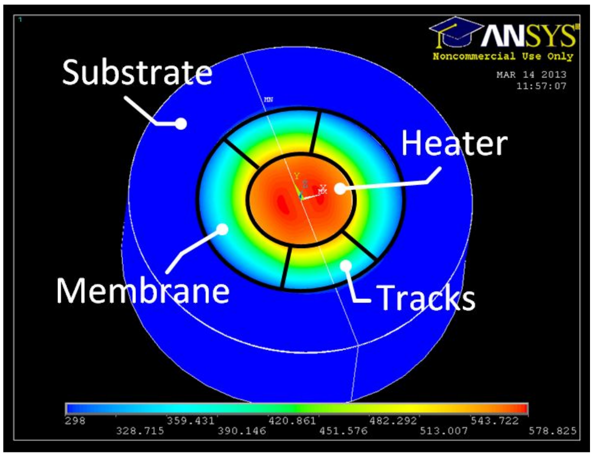

Figure 4: Microhotplate temperature [K] profile simulated with software Ansys.

EXPERIMENTAL

Here NMP-dispersed exfoliated graphene dispersions in DI water were deposited by non-contact, ambient temperature micro-inkjet printing (Microdrop Tech.) (Figure 5a), fitted with a PC controlled piezo stage and a strobe monitoring unit, used to verify the drop stability and the absence of satellite drops (Figure 5b), which might detrimentally affect the process reproducibility. The non-contact process and the micro controlled positioning guarantee the integrity of the fragile membranes and a very accurate graphene deposition (Figure 5c), exclusively over the gold inter-digitated electrodes (IDEs). Drops had a volume of approximately 10^2 pL. Samples were coated with 7×10^4 drops. NMP (N-methyl-pyrrolidone) is an organic dipolar solvent characterized by a relatively high boiling point (202°C) and low evaporation rate; if compared to other common solvent such as DI water or isopropanol (IPA). These intrinsic properties of the solvent created some initial problems for the deposition process. In fact, a continuous dispensing of the solution generated a 2 mm diameter deposition area (an order of magnitude bigger than our targeted area). It has been possible to reduce the extension of the deposition area by alternating streams of drops with pauses, and running the process heating the chips with an external heater at a temperature of about 80°C. The developed protocol increased the deposition time (*ca*. 3 hours, per chip, against the initial *ca*. 2 hours), but ensured an accurate control of the dimension of the deposition area.

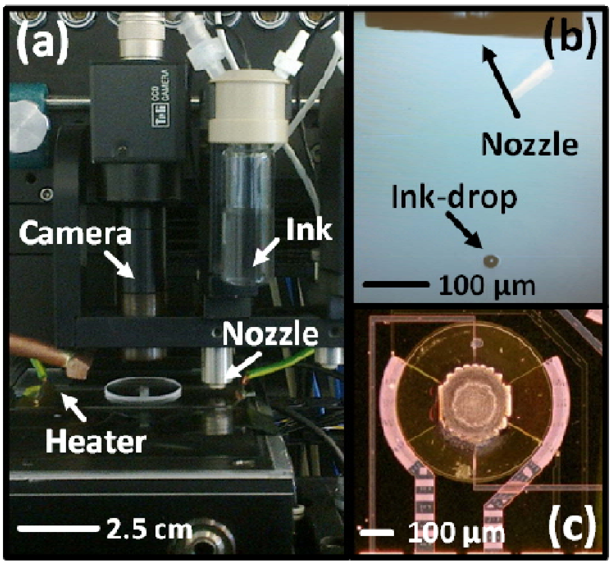

Figure 5: Photograph of micro inkjet deposition system (a) and micrographs of inkjet printer during deposition (b) and graphene coating IDEs/p+-Si heater (c).

The inkjet-deposited graphene was analysed using 633 nm excitation Raman spectroscopy and compared with other deposited carbon-based nanomaterials: multi-walled carbon nanotubes (MWCNTs), carbon nanoparticles (CNPs), C60, and graphene oxide. Figure 6 shows the Raman spectra for the graphene studied here; it can be seen that it is not perfect graphene but has defects. We believe that these defects (dangling bonds) in the graphene could promote a higher sensitivity to reactive gases, such as NO_2.

To study the selectivity of the graphene, we sputtered nanoclusters of different metals (Rh and Au) on the inkjet graphene layer. Semi-processed sensor dies with inkjet-printed graphene underwent a reactive plasma treatment before metal decoration. The treatment was performed at a pressure of 0.1 Torr, using a power of 15 W, while the processing time was adjusted to 1 min. A controlled flow of oxygen was introduced inside the chamber, which gave rise to functional oxygen species attached to the surface of graphene. This helps the nucleation and anchoring of metal clusters during the decoration step. The Au and Rh sputtering conditions for power and duration were 30 W for a period of 7 s and 60 W for 10 s, respectively. Previous work has shown that this could improve the gas sensitivity of CNTs [4]. The size of metal nanoparticles is about 2 nm and this size remains stable even when the nanomaterials are thermally-treated at 350ºC for one hour.

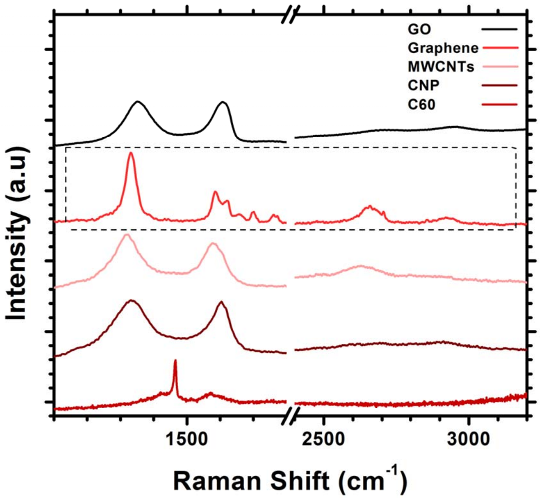

Figure 6: 633 nm excitation Raman spectra of carbon-based materials on our SOI micro-hotplates. The high-lighted spectrum is of the ink-jet deposited graphene reported here.

Figure 7 shows the metal decoration of multi-walled CNTs employing the same conditions described above.

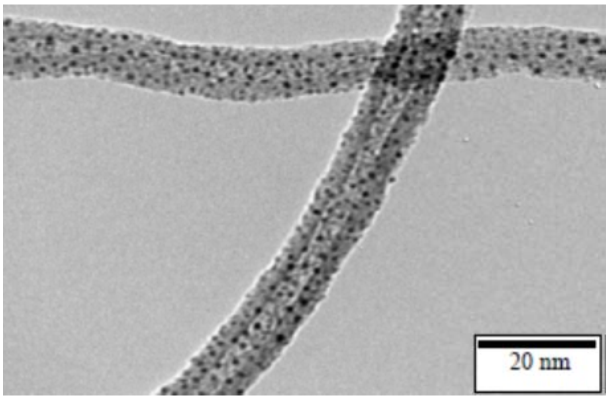

Figure 7: Au-decorated CNT employing the same techniques used here to treat inkjet-printed graphene. Nanoparticle size is about 2 nm.

The fabricated chips were, then, in-house wedge bonded to Au plated TO5 packages using 25.4 µm Au wire and a thermally conductive adhesive.

RESULTS

Figure 8 shows the resistance of the pure graphene and Rh and Au nanoparticle functionalised graphene. Reversible responses to 100 ppb pulses of NO_2 at a temperature of 150°C are clearly seen.

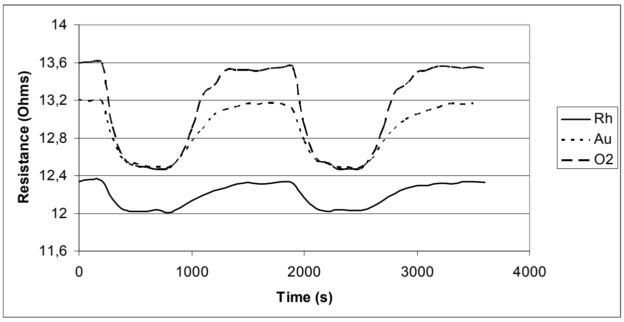

Figure 8: Response of pure and Rh/Au functionalised graphene chemiresistors to 100 ppb of NO_2 at a device temperature of 150ºC.

Similarly, Figure 9 shows the response at 300°C. The changes observed here for pure graphene are higher than chemiresistors functionalized by Rh and Au.

The response ℵ of the gas sensors can be defined by the fractional change in resistance,

$$\aleph = \frac{(R_{Air} - R_{NO_2})}{R_{Air}} \tag{1}$$

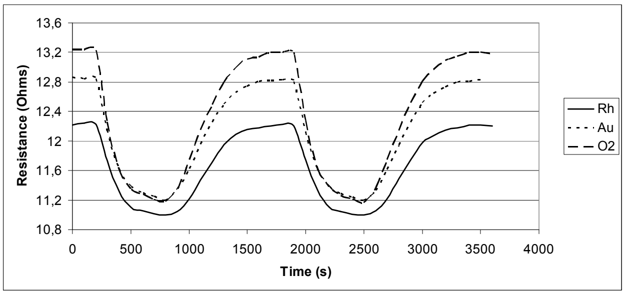

Figure 9: Response of pure and Rh/Au functionalised graphene chemiresistors to 100 ppb of NO_2 at a device temperature of 300ºC.

Table 1 summarizes the responses of our SOI graphene sensors to 100 ppb of NO_2 in air. The response at 300°C is about four times that at room temperature and twice that at 150ºC. In addition the response time is about ×3 slower at 50°C than at 300°C.

Table 1: Percentage response of graphene SOI sensors as defined by $(R_{air}-R_{NO2}/R_{air})\times 100$ for a pulse of 100 ppb of NO_2 in air at different temperatures.

Temp (°C)	**Rh doped**	**Au doped**	**Undoped**
300	10.16	12.88	15.71
150	2.68	5.35	8.39
30	1.23	3.00	4.88

The response time of a sensor can be conveniently defined by its value at 90% of the steady-state signal (τ_{90}). The τ_{90} values have been determined for a series of NO_2 pulses and at three different temperatures. Figure 10 shows a plot of the response time together with its response for an undoped graphene sensor. The response time falls to *ca*. 180 s at an operating temperature of 300°C. This is still a relatively slow response time and may be associated with the fact that the graphene is thick.

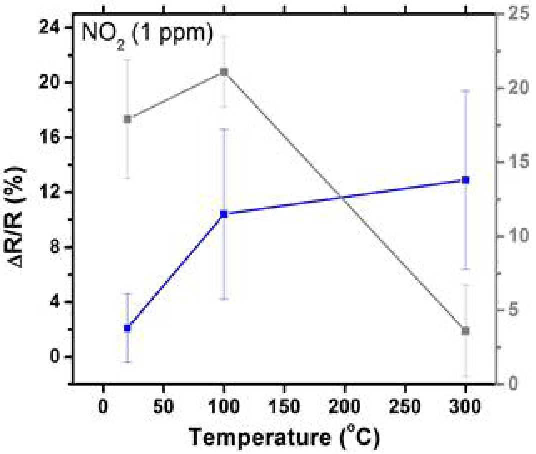

Figure 10: Response and response time of pure graphene chemiresistor to 1000 ppb of NO_2 in air at several device temperatures.

CONCLUSIONS

To conclude, we have developed low-cost SOI CMOS gas sensors employing simple ink-jet printed graphene as a gas sensitive layer. The graphene was functionalized with metallic nanoparticles, however this did not yield higher gas sensitivity. The graphene sensors show high sensitivity of approximately 0.1% per PPB to NO_2.

Further work is underway exploring other metals as well as cross-sensitivity to other gases.

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