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# High sensitive gas sensors realized by a transfer-free process of CVD graphene

F. Ricciardella<sup>1</sup>, S. Vollebregt<sup>1</sup>, T. Polichetti<sup>2</sup>, B. Alfano<sup>2,3</sup>, E. Massera<sup>2</sup> and P.M. Sarro<sup>1</sup>

<sup>1</sup>Delft University of Technology, Department of Microelectronics, Delft, The Netherlands

<sup>2</sup>ENEA UTTP-MDB, Portici (Naples), Italy

<sup>3</sup>University of Naples “Federico II”, Department of Physics, Naples, Italy

[filiberto.ricciardella@gmail.com](mailto:filiberto.ricciardella@gmail.com)

**Abstract**—The work herein presented investigates the behavior of graphene-based gas sensors realized by using an innovative way to prepare graphene. The sensing layer was directly grown by chemical vapor deposition on pre-patterned CMOS compatible Mo catalyst and then it was eased on the underlying SiO<sub>2</sub> through a completely transfer-free process. Devices with different geometries were designed and tested towards NO<sub>2</sub> and NH<sub>3</sub> in environmental conditions, i.e. room temperature and relative humidity set at 50%. Furthermore, these gas sensors were also calibrated, resulting in the ability to detect concentrations down to 240 ppb and 17 ppm of NO<sub>2</sub> and NH<sub>3</sub>, respectively. These results are in agreement with the best performances reported in literature for graphene-based sensors. They not only confirm the successful devices fabrication through the transfer-free approach, but also pave the route for large-scale production of MEMS/NEMS sensors.

**Keywords**—graphene-based gas sensors; environmental conditions; chemical vapor deposition; transfer-free process

## I. INTRODUCTION

After the discovery of graphene since 2004 [1], large research efforts have been provided to grow this so-called “wonder material”, encompassing liquid exfoliation, epitaxy from crystalline SiC wafers and chemical vapour deposition (CVD) [2]. However, in order to make this material truly available for applications, a main bottleneck needs to be overcome, i.e. the unavoidable step of the material transfer from the growth substrate to the target one, that usually needs to be covered by an insulating thin film. The transfer process is mainly carried out through a carrier polymer [3-4]. Because of transfer medium residues or contamination, this step can dramatically affect the graphene layer quality and, in turn, the device performance [5-6]. However, in the gas sensing field, by using CVD grown graphene transferred via the conventional wet-transfer process, very low gas concentrations have been detected. For instance, Kumar et al. [7] have recently reported graphene-based gas sensors transferred on paper that reach NO<sub>2</sub> concentration down to 300 ppb whilst Mortazavi Zanjani et al. [8] have introduced resistive sensors able to detect down to 2 ppm of NH<sub>3</sub>.

In this paper, we demonstrate the effective potential the innovative transfer-free process we have recently developed [9] offers to fabricate gas sensors achieving the best performances reported in literature without the transfer process complexity [7-8, 10-13]. The overall behaviour of devices operating in environmental conditions, i.e. room temperature (RT) and

relative humidity (RH) set at 50%, and having two different geometries, in terms of sensing area, is addressed. In particular, calibrations towards oxidant and reducing gas, such as NO<sub>2</sub> and NH<sub>3</sub>, are reported, achieving detectable concentrations down to 240 parts-per-billion (ppb) and 17 parts-per-million (ppm), respectively.

## II. EXPERIMENTAL

The devices were fabricated on 4” Si (100) wafers covered by thermally grown SiO<sub>2</sub> (90 nm). Then, as reported in the schematic flow chart in Fig. 1, a Mo thin film of 50 nm is sputtered from a pure (99.95%) Mo target (Fig. 1a). Dry etching with SF<sub>6</sub>, combined with a photo-lithographic resist layer, was used to pattern the Mo layer.

Graphene was grown on the patterned Mo catalyst in an AIXTRON BlackMagic Pro at 1000 °C, using Ar/H<sub>2</sub>/CH<sub>4</sub> as feedstock at a pressure of 25 mbar (Fig. 1b). After the CVD graphene deposition, the Mo catalyst was etched by means of a phosphoric acid solution and subsequently the wafers were rinsed and spin-dried. After the Mo etching, the released graphene film adhesion to the SiO<sub>2</sub> was facilitated by the anchoring of the graphene film at the edges of the pre-patterned catalyst. (Fig. 1c). As last step, Cr/Au (10/50 nm) electrical contacts were evaporated using a lift-off process (Fig. 1d).

The devices were electrically characterized by a semi-automatic probe-station with an Agilent 4156C semiconductor parameter analyzer. The tests on the gas sensors were performed in a Gas Sensor Characterization System (GSCS, Kenosistec equipment) setting temperature and RH at 22 °C and 50%, respectively.

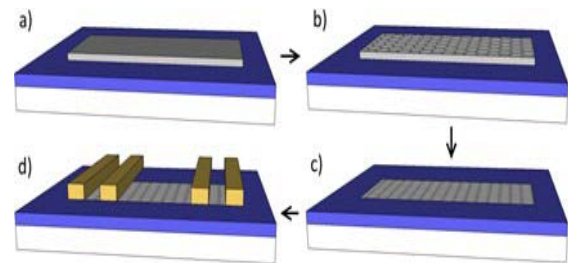


Fig. 1. Schematic flow chart of the fabrication process: a) deposition and patterning of the Mo layer on Si substrate covered by 90 nm SiO<sub>2</sub>; b) CVD grown graphene on Mo; c) wet etching of the Mo layer; d) deposition of Cr/Au electrodes using a lift-off process.

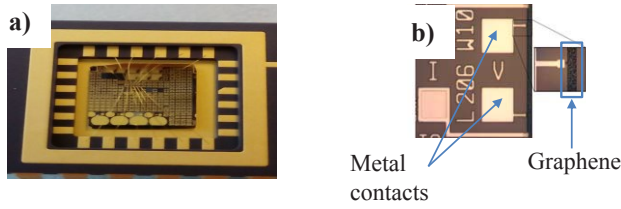


Fig. 2. Picture of wire-bonded die on the chip and (b) image of the electrical structure consisting in a graphene line-width of 10  $\mu\text{m}$  with close-up of Au-graphene contact.

Different gases concentrations were obtained by a programmable mass flow controllers (MKS). During the measurements, sensors were biased at a constant DC voltage equal to 1V with a Precision Power Supply TTI QL355T.

### III. RESULTS AND DISCUSSIONS

As reported in [9], the Raman analysis performed during the sensors fabrication process shows that there is no substantial difference in the graphene at the different stages: on Mo after growth, after Mo etching and after gold patterning. This indicates the effectiveness of the transfer-free process and the good quality of the obtained graphene film.

Based on the fabrication process depicted in Fig. 1, devices consisting of graphene resistors with a width of 2, 5 and 10  $\mu\text{m}$  were characterized through four point probe electrical measurements. The realized devices (Fig. 2b) were mounted in a 24 pins chip and wire bonded (Fig. 2a) for testing in the gas system.

From the I-V characteristics (Fig. 3), the ohmic contact between the Cr/Au and graphene layer is clearly demonstrated and, taking into account the device dimensions, the sheet resistance can be determined to be  $\sim 830 \Omega/\text{sq}$ . Devices with lines 10 and 5  $\mu\text{m}$  (in the following addressed as Device 1 and 2, respectively) were tested in GSCS in the presence of  $\text{NO}_2$  and  $\text{NH}_3$  gas, which act as electron acceptor and donor, respectively. Fig. 5 shows the current dynamic behaviour of the

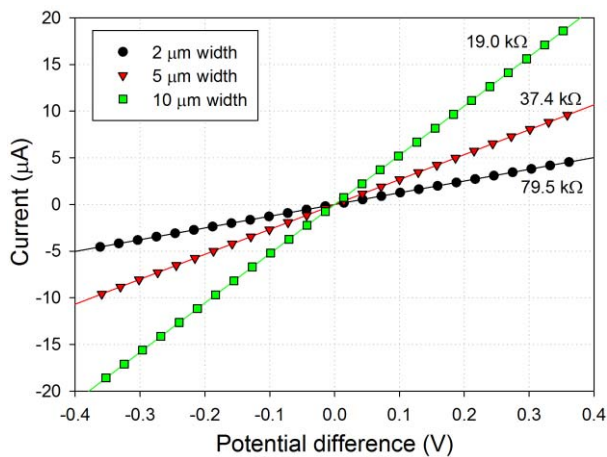


Fig. 3. I-V characteristics of graphene resistors fabricated with different widths (length 206  $\mu\text{m}$ ). The ohmic contact can be argued from the linear response and  $R_{\text{sheet}} = 830 \Omega/\text{sq}$  can be determined.

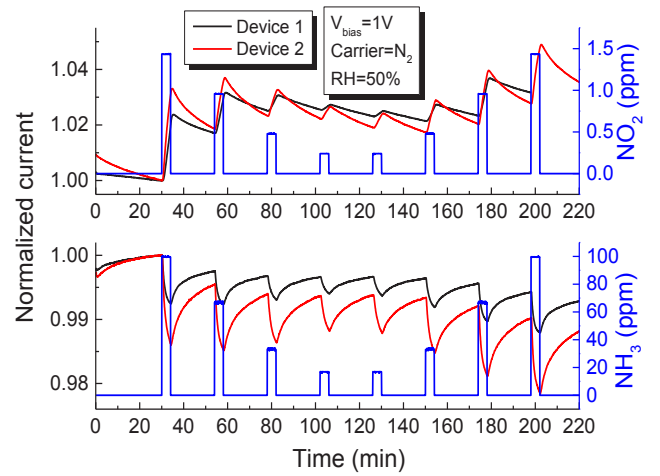


Fig. 4. Current dynamic behavior of sensors upon exposure to sequential  $\text{NO}_2$  and  $\text{NH}_3$  pulses (blue rectangles) at different concentrations ranging from 0.24 up to 1.44 ppm and from 17 up to 100 ppm, respectively. Each exposure step is 4 min long, preceded and followed by 20 min long baseline and recovery phases, respectively, in  $\text{N}_2$  atmosphere. The current is normalized to the value during the gas inlet of the first pulse exposure.

sensors upon exposure to sequential target gas pulses, highlighted as blue rectangles.

The different concentrations range from 0.24 till to 1.44 ppm and from 17 till to 100 ppm, for  $\text{NO}_2$  and  $\text{NH}_3$  gas, respectively. Each exposure step is 4 min long, preceded and followed by 20 min long baseline and recovery phases, respectively, in  $\text{N}_2$  atmosphere. The current responses are normalized to the value during the gas inlet of the first pulse exposure. Furthermore, the repeatability of the chemi-resistors behaviour is also addressed since the test protocol is set as sequential rise up and down of the gas concentrations. As reported in the panels of Fig. 4, the changes in current are roughly the same for decreasing and increasing gas concentration. For both gases the current percentage variation of the ramp down phase are plotted as function of the gas concentration (Fig. 5), where  $I_0$  represents the current value at the gas inlet for each pulse. From the linear trend of the calibration plots, the sensitivity, corresponding to the curve slope, can be extrapolated. As reported in Table I, comparing the sensors performance, Device 2 results to be more sensitive with respect to Device 1 for both gases. This can be explained by the fact that, for an equal number of graphene layers, the sensitivity can be increased by reducing the sensing exposure area. This is the case for Device 2 that has an area reduced of roughly half with respect to Device 1. Also, these findings suggest that the graphene basal plane might be less sensitive with respect to flake edges, that represent a kind of defects for the crystal [14]. Therefore, when reducing the sensitive area of the sample, the density of the edge defects is considerably higher and consequently the more reactive part towards the gases is enlarged. Given the reproducibility and accuracy the developed fabrication process offers, the sensors sensitivity can be modulated by tuning the device geometry.

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## REFERENCES

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. A. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films," *Science*, vol. 306, pp. 666–669, October 2004.
- [2] F. Bonaccorso, A. Lombardo, T. Hasan, Z. Sun, L. Colombo, and A. C. Ferrari, "Production and processing of graphene and 2d crystals". *Mat. Today*, vol. 15, pp. 564-589, December 2012.
- [3] J. Y. Choi, "A stamp for all substrates," *Nat. Nanotechnol.*, vol. 8, pp. 311-312, May 2013.
- [4] J. Song, F. Y. Kam, R. Q. Png, W. L. Seah, J. M. Zhuo, G. K. Lim, P. K. H. Ho, L. L. Chua, "A general method for transferring graphene onto soft surfaces," *Nat. Nanotechnol.*, vol. 8, pp. 356-362, May 2013.
- [5] Y. C. Lin, C. Jin, J. C. Lee, S. F. Jen, K. Suenaga, and P. W. Chiu, "Clean Transfer of Graphene for Isolation and Suspension," *ACS Nano*, vol. 5, pp. 2362–2368, February 2011.
- [6] W. Zhu, T. Low, V. Perebeinos, A. A. Bol, Y. Zhu, H. Yan, J. Tersoff, and P. Avouris, "Structure and Electronic Transport in Graphene Wrinkles," *Nano Lett.*, vol. 12, pp. 3431–3436, May 2012.
- [7] S. Kumar, S. Kaushik, R. Pratap, and S. Raghavan, "Graphene on Paper: A Simple, Low-Cost Chemical Sensing Platform," *ACS Appl. Mater. Interfaces*, vol. 7, pp. 2189–2194, January 2015.
- [8] S. M. Mortazavi Zanjani, M. M. Sadeghi, M. Holt, Sk. F. Chowdhury, L. Tao, and D. Akinwande, "Enhanced sensitivity of graphene ammonia gas sensors using molecular doping," *Appl. Phys. Lett.*, vol. 108, pp. 033106, January 2016.
- [9] S. Vollebregt, B. Alfano, F. Ricciardella, A. J. M. Giesbers, Y. Grachova, H. W. van Zeijl, T. Polichetti, and P. M. Sarro, "A transfer-free wafer-scale CVD graphene fabrication process for MEMS/NEMS sensors," *IEEE 29th International Conference on Micro Electro Mechanical Systems (MEMS)*, pp. 17-20, January 2016.
- [10] E. Llobet, "Gas sensors using carbon nanomaterials: A review," *Sens. and Act. B: Chem.*, vol. 179, pp. 32-45, March 2013.
- [11] W. Yuan and G. Shi, "Graphene-based gas sensors," *J. Mat. Chem. A*, vol. 1, pp.10078-10091, June 2013.
- [12] F. Ricciardella, E. Massera, T. Polichetti, M. L. Miglietta, and G. Di Francia, "A calibrated graphene-based chemi-sensor for sub parts-per-million NO<sub>2</sub> detection operating at room temperature," *Appl. Phys. Lett.*, vol. 104, pp. 183502, May 2014.
- [13] B. Alfano, T. Polichetti, M. Mauriello, M. L. Miglietta, F. Ricciardella, E. Massera, and G. Di Francia, "Modulating the sensing properties of graphene through an eco-friendly metal-decoration process," *Sens. and Act B: Chem.*, vol. 222, pp. 1032-1042, January 2016.
- [14] Y.-H. Zhang, Y.- B. Chen, K.- G. Zhou, C.- H. Liu, J. Zeng, H.- L. Zhang, and Y. Peng, "Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study," *Nanotechnology*, vol 20, pp. 185504, April 2009.

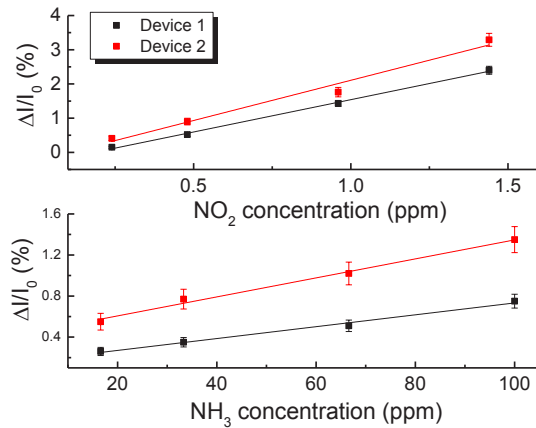


Fig. 5. Calibration curves of graphene-based sensors towards NO<sub>2</sub> and NH<sub>3</sub>. The current percentage variations are plotted as function of concentration, where I<sub>0</sub> represents the current value at the gas inlet for each gas pulse depicted in Fig. 4.

TABLE I. DEVICES SENSITIVITY UPON EXPOSURE TO NO<sub>2</sub> AND NH<sub>3</sub>

	Sensitivity (ppm <sup>-1</sup> )	
	NO <sub>2</sub>	NH <sub>3</sub>
Device 1	1.9·10 <sup>-2</sup>	5.8·10 <sup>-5</sup>
Device 2	2.4·10 <sup>-2</sup>	9.3·10 <sup>-5</sup>

## IV. CONCLUSIONS

In this work gas sensors realized by using a completely transfer-free process of chemical vapour deposition graphene were presented. On pre-patterned CMOS compatible Mo catalyst, graphene based chemi-resistors were fabricated according to two different geometries, in terms of graphene line width: 5 and 10 μm. The devices were tested in environmental conditions towards oxidant and reducing gases, such as NO<sub>2</sub> and NH<sub>3</sub>, in the range 0.24 – 1.44 ppm and 17 - 100 ppm, respectively. In these windows of exposure, the sensors were calibrated and the performances were compared. A linear behaviour of the current variation as function of the gases concentration was determined for both Device 1 and Device 2. The latter one, having a sensing area reduced by half with respect to the former one, showed a higher sensitivity upon exposure towards both gases, indicating that the sensitivity can be modulated by varying the geometry of the device exposure area.