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An innovative approach to overcome saturation and recovery issues of CVD graphene-based gas sensors

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In this work, we present an innovative method which enables to solve fundamental limitations affecting graphene-based chemi-sensors operating under environmental conditions, namely the lack of signal saturation and the scarce recovery after the detection step. The method, which exploits the differential current instead of the current itself, is validated by applying it on different devices having an exposed area equal to $512 \mu\text{m}^2$. The analysis is performed by adopting nitrogen dioxide (NO_2) as target gas in the range from 0.12 ppm to 1.5 ppm. The approach reliability is further confirmed by performing sensing tests towards NO_2 with the relative humidity set at two different levels, 30% and 50%.

Graphene-based gas sensors; differential calibration method; NO_2 ; environmental conditions; chemical vapor deposition; transfer-free process

I. INTRODUCTION

Graphene, a single sheet of carbon atoms, represents nowadays one of the most suitable candidates for gas sensors operating under environmental conditions, i.e. at room temperature (RT) and relative humidity (RH). In fact, the graphene highest surface-to-volume ratio ($\sim 2600 \text{ m}^2/\text{g}$), the strong stability and, especially, the interaction of the target gas with single surface atom are features that drive the material to be adopted as the ideal sensing layer for this kind of applications [1-4]. However, graphene-based gas-sensors, similarly to the largest class of solid state gas-sensors operating at ambient conditions, are well known to be affected by the hindrances due to the excessively slow rate of desorption of the reactive gases [3] and to the absence of signal saturation [46]. The first issue is particularly more evident if no external source of energy is supplied to encourage the molecules removal, as for instance ultraviolet light irradiation [7], thermal treatment [8, 9] or an electric field [10]. For the signal saturation issue, the mentioned drawback has been observed since the first work reporting a graphene-based gas sensor [10]. In that paper, the author claimed that even “during long exposures to small (ppm) concentrations of active gases the devices did not exhibit saturation in the detected signal indicating that the effect of chemical doping in graphene is cumulative. A partial saturation can be observed if the sensors are exposed to a limited volume of the chemicals rather than a constant flow” [10]. Here we report on an innovative approach that, exploiting the differential current, allows to analyze the performance of graphene-based gas sensors operating under environmental conditions. In addition, thanks to the differential analysis, we also prove that the saturation and recovery issues can be

solved. Due to the strong interaction between NO_2 and water, especially in terms of solubility [11], we further validate the method reliability through tests performed at different levels of RH, i.e. 30% and 50%.

II. EXPERIMENTAL

The graphene-based gas sensors adopted in this study were fabricated on 4” Si (100) wafer covered by thermally grown SiO_2 (90 nm). A thin film of Mo (50 nm) was sputtered from a pure (99.95%) Mo target. Afterwards, dry etching combined with a photo-lithographic resist layer was used to pattern the Mo layer, as reported in our previous work [12]. The graphene growth on the patterned Mo catalyst was carried out in an AIXTRON BlackMagic Pro at 1000°C , using $\text{Ar}/\text{H}_2/\text{CH}_4$ as feedstock at a pressure of 25 mbar. The Mo catalyst was then etched away following the transfer-free process (TFP) we developed [12] and the graphene film adhered to the SiO_2 . Evaporated Cr/Au (10/100 nm) electrical contacts were defined on the top of graphene film using a lift-off process.

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. A second set of measurements were accomplished setting the RH to 30%.

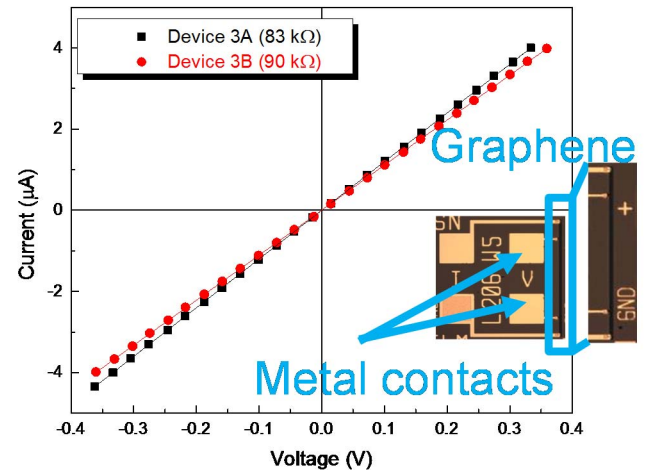


Fig. 1. I-V characteristics of the graphene-based resistors reported in the inset.

III. RESULTS AND DISCUSSIONS

As reported in [12, 13], the TFP does not deteriorate the high quality of the graphene films. Furthermore, thanks to the TFP process, large scale production of many hundreds of devices per wafer can be obtained with tightly controlled dimensions (devices having width of 2, 5 and 10 μm). In order to pursue miniaturization of these gas sensors, here we focus on the smallest size devices, namely 2 μm width resistors.

Once the Ohmic contact between the Cr/Au and graphene layer was proved through the I-V characteristics (Fig. 1) on two different devices (in the following addressed as Device 3A and 3B, respectively), the resistors were tested in GSCS towards NO_2 . In our previous work, in fact, we demonstrated the stronger selectivity of pristine graphene towards NO_2 operating under environmental conditions with respect to other

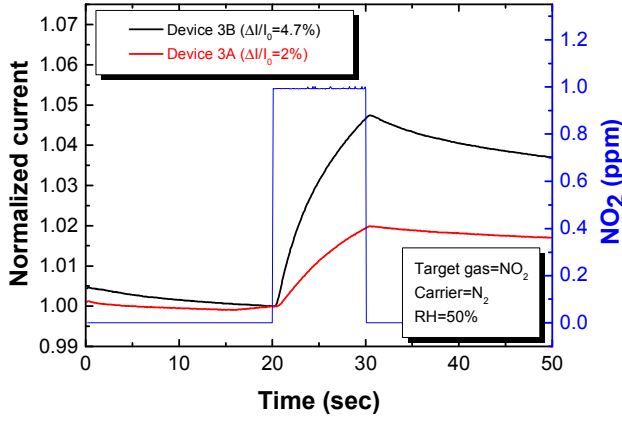


Fig. 2. Current dynamic behavior of sensors upon exposure to 1 ppm of NO_2 (blue rectangle). The step is 10 min long, preceded and followed by 20 min long baseline and recovery phases, respectively, in N_2 atmosphere.

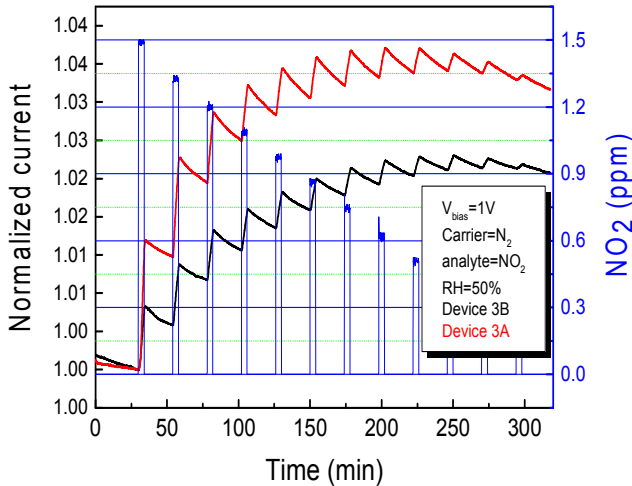


Fig. 3. Current dynamic behavior of sensors upon exposure to sequential NO_2 pulses (blue rectangles) at different concentrations ranging from 0.12 up to 1.5 ppm. Each exposure step is 4 min long, preceded and followed by 20 min long baseline and recovery phases, respectively, in N_2 atmosphere.

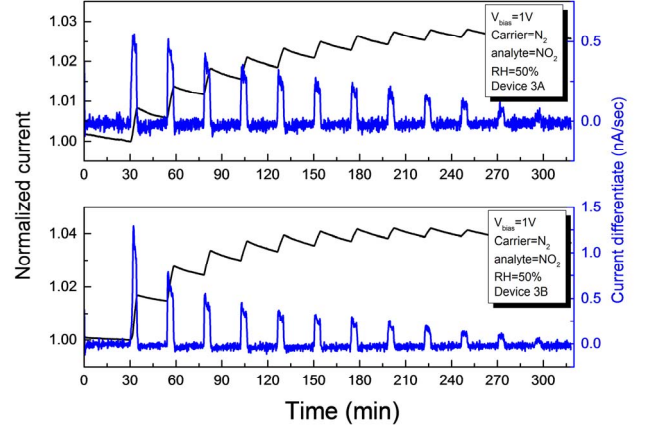


Fig. 4. Current dynamic behavior (black line) and differential current (blue line) for Device 3A (upper panel) and Device 3B (upper panel), respectively.

analytes [13]. In Fig.2 the current variation $\Delta I/I_0$ upon a single exposure at 1 ppm of NO_2 (blue rectangle) is reported, where I_0 and I represent the current values at the gas inlet and outlet, respectively.

The plots, highlighting that both sensors are able to detect the analyte, show overall the same kinetics during the adsorption step, the lack of signal saturation as well as a scarce recovery. However, a slight difference between the two devices, especially in terms of absolute value of current variation, can be observed. The same features are also noticed in Fig., where the current dynamic behaviour upon exposure to sequential pulses for concentrations ranging from 0.12 ppm to 1.5 (in the following addressed as Test 2) are reported.

In order to overcome these issues so to be able to compare the sensor behaviors, the approach developed in our previous work [14] has been applied. This method basically consists in taking into account the differential current instead of the current itself. The former one results to be a more powerful parameter than the latter one, especially for gas sensors that continuously integrate gas molecules and show signal growth. In 4 the current (black line) and the differential current (blue line) are reported, respectively, for Devices 3A (upper panel) and 3B (lower panel).

By plotting the maxima of the differential current (Fig.) [14], the outcomes display a strong linearity as a function of NO_2 concentration.

The slope values of the fitting curves in Fig. 5, named as differential sensitivity, clearly indicate the reliability of this fast investigation method. The effectiveness of the approach is further proved by the fact that the signal saturation and the lack of recovery are negligible, since the differential signal is only taken into account. Also, it is immediate applicable, allowing to compare simultaneously a large number of device performances, also affected by device-to-device variations. In order to further validate the approach effectiveness, Test 2 was performed on both sensors towards NO_2 by varying the RH level from 50% to 30%. NO_2 and water, in fact, are strongly interacting, especially in terms of solubility [11]. In Table I, the differential sensitivity extrapolated from tests performed at two values of RH for Device 3A and 3B are

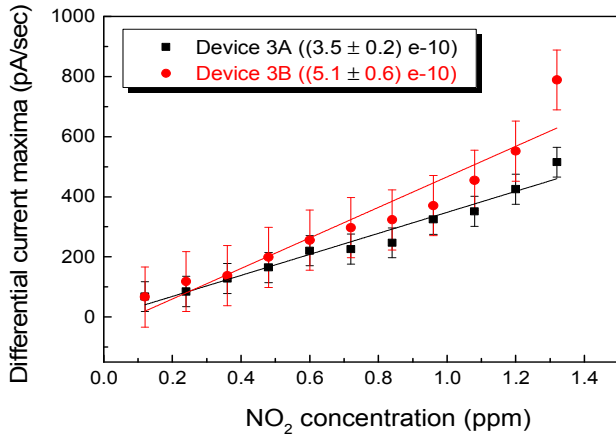


Fig. 5. Maxima of the differential curves for Device 3A (black points) and Device 3B (red points) collected at different NO₂ concentrations as obtained in Fig. 4. The straight lines represent the fitting curves.

TABLE I. DIFFERENTIAL SENSITIVITY UPON EXPOSURE TO NO₂ AT TWO DIFFERENT LEVELS OF RELATIVE HUMIDITY

	Differential sensitivity (10 ⁻¹⁰ A/sec)	
	RH= 30%	RH= 50%
Device 3A	1.9 ± 0.2	3.5 ± 0.2
Device 3B	3.6 ± 0.4	5.1 ± 0.6

compared. On the basis of the values obtained setting RH at 30%, once more the approach proves to be reliable, paving the route towards a new way to treat solid state gas sensors affected by absence of signal saturation and scarce recovery.

IV. CONCLUSIONS

In this work, a new approach to analyze the performance of graphene-based gas sensors operating under environmental conditions was presented. The chemi-resistors, having an area of 512 μm², were prepared on pre-patterned CMOS compatible Mo catalyst and tested towards NO₂ in the range 0.12 – 1.5 ppm. As the investigated graphene-based gas sensors showed no signal saturation and scarce recovery at room temperature, similarly to the integrating sensors, the developed approach consisted in exploiting the differential current. Thanks to this method, not only slight device-to-device variations were negligible, but also the saturation and the recovery issues were overcome. Also, the method is immediate applicable to compare simultaneously a large number of sensors' performance. The method reliability, further validated by testing the sensors towards NO₂ at a different value of RH (30%), paves an innovative route to overcome severe limitations encountered in graphene-based gas sensors, and more generally in large class of integrating sensors.

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