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Functionalisation of Multi-Layer Graphene-Based Gas Sensor by Au Nanoparticles †

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Abstract: A novel gas sensor based on multi-layered graphene (MLG) functionalised with gold nanoparticles (Au-NPs) is presented. We demonstrate for the first time that: (1) the signal saturates during the analyte exposure, something which does not occur in the pristine material and in graphene-based gas sensors in general; (2) the sign of the device current response is inverted. MLG is grown by chemical vapour deposition on pre-patterned CMOS-compatible Mo catalyst. The sensor is fabricated directly on the growth substrate, without any transfer of MLG. The Au-NPs are later deposited from an aerosol on the sensor at a specific controlled location, mitigating any additional patterning steps. The functionalised sensor is tested with 1 ppm (part-per-million) of NO_2 at room temperature.

Keywords: gas sensors; graphene; functionalisation; nanoparticles

1. Introduction

Graphene retrieves much attention as a promising material for gas sensing applications, because of its potential ppb-level (part-per-billion) sensitivity at room temperature (RT) and low 1/f noise. Graphene-based gas sensors working at RT exhibit enhanced sensitivity towards many gas molecules, e.g., NO_2, NH_3, and H_2O, thanks to the ambipolar nature of this material [1].

However, these gas-sensors are still affected by low selectivity, poor recovery and absence of response saturation, hampering their application in commercial devices. Functionalising the graphene with molecules, dopants or nanoparticles has been proposed as a method to improve selectivity by changing the electrical properties of the graphene. For instance, Au-NPs deposited on single-layer graphene have been shown to change the electrical doping, with a dependence on the coverage of the NPs [2]. In this work, we experimentally show that Au-NPs can effectively reverse the gas sensing behaviour of multi-layered graphene (MLG). Moreover, we present for the first time a saturating MLG-based gas sensor, working at RT.

2. Methods

The chemi-resistive gas sensor is illustrated in Figure 1a. The sensing layer was grown using chemical vapour deposition (CVD) at around 1000 °C on a pre-patterned Mo catalyst. The device was prepared on the same substrate where MLG was selectively grown in pre-determined locations, avoiding the need for graphene transfer [3]. The Au-NPs, used to functionalise the graphene, were selectively deposited by inertial impaction from a solvent-free aerosol stream of Au-NPs generated by spark ablation in a commercially available NP generator. The sensor with pristine and functionalised MLG was exposed to 1 ppm of NO_2 at RT in dry N_2, while biased at 1 V. Pristine material was previously found to be sensitive to NO_2 [4].

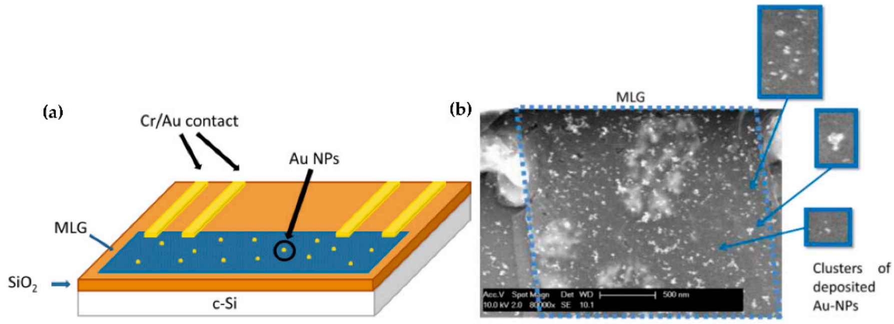

Figure 1. (**a**) Device schematic, on the multi-layered graphene (MLG) bar (206 µm long, 10 µm wide) where the gold nanoparticles are deposited. The Cr/Au contacts represent the pads of the resistor; (**b**) SEM image of a portion of the MLG-based device (enclosed in the dashed frame) after the Au-NPs' deposition. The clusters of Au-NPs are shown in the blue frames.

3. Results and Discussion

Scanning electron microscope (SEM) images (Figure 1b) show small clusters of Au-NPs. The NPs homogenously cover around 7% of the device area, as determined from the SEM images. Pristine and functionalised devices show an Ohmic behaviour. Due to the sparse level of NP distribution, the graphene sheet resistance decreases only by ~5% from 1 kΩ to 0.96 kΩ.

Figure 2a reports the gas test before the NP deposition. NO_2 is an electron-acceptor gas. The current increase indicates the p-doping of the pristine MLG. The signal keeps rising until the NO_2 flow is stopped, demonstrating the absence of a steady-state in pristine MLG.

After the functionalisation, the chemical bonding between the MLG and Au-NPs causes n-type doping of the MLG, which results in a decrease in current upon NO_2 exposure (Figure 2b). Interestingly the signal then demonstrates saturation. The $\Delta I/I_0$ is also positively affected by the NPs presence, indicating enhanced sensitivity. These results demonstrate that selectively deposited NP can dramatically change the gas sensing behaviour of graphene, enabling new ways to functionalise graphene-based gas sensors.

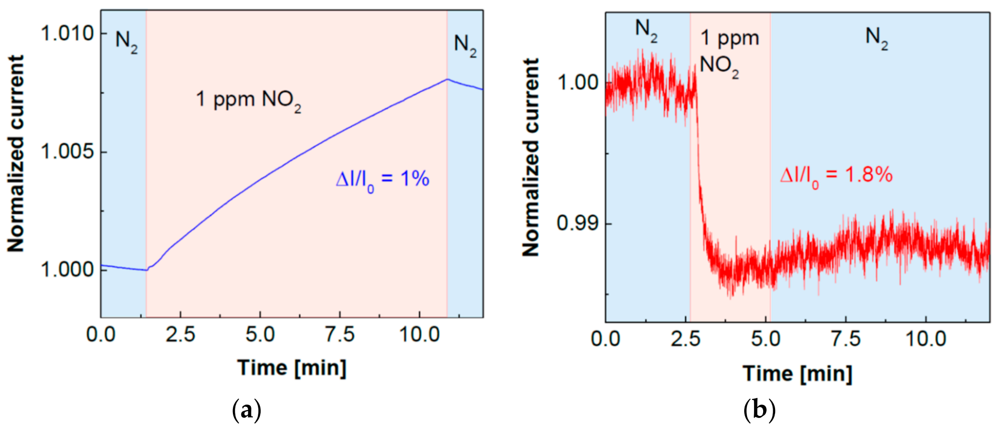

Figure 2. Dynamic current behaviour of the sensors, where the current is normalised to the value at the gas inlet. (**a**) pristine sensor; (**b**) sensor functionalised with Au-NP.

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