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Proceedings

Low Temperature CVD Grown Graphene for Highly Selective Gas Sensors Working under Ambient Conditions [†]

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Abstract: In this paper we report on gas sensors based on graphene grown by Chemical Vapor Deposition at 850 °C. Mo was used as catalyst for graphene nucleation. Resistors were directly designed on pre-patterned Mo using the transfer-free process we recently developed, thus avoiding films damage during the transfer to the target substrate. Devices operating at room temperature and relative humidity set at 50% were tested towards NO₂. The sensors resulted to be highly specific towards NO₂ and showed current variation up to 6%. The performances were compared with those of gas sensors based on graphene grown at 980 °C, which represents the usual growth temperature for such material. The findings show that by lowering the graphene growth temperature and consequently the energy consumptions the sensing benefits of these devices are still preserved.

Keywords: gas sensors; NO₂; environmental conditions; graphene; chemical vapor deposition; transfer-free process

1. Introduction

Among the many attractive properties graphene has, the strong stability, the highest surface-to-volume ratio (~2600 m² g⁻¹) and the interaction with only the surface atoms, make graphene the ideal candidate for gas sensors operating in ambient conditions [1]. CVD graphene, in particular, reveals itself particularly promising in terms of high quality and large scale production [2]. However, for practical applications, the bottleneck related to the CVD technique is inherent to the graphene transfer from the catalyst substrate to the target one [3]. On this regard, we have recently reported a transfer-free process (TFP) that prevents any issue related to the graphene transfer [4]. In our previous work, graphene-based gas sensors prepared through TFP were found to be able to achieve extremely low limit of detection (LOD), in the range of a few hundred ppb of NO₂, and resulted scarcely sensitive towards NH₃ [4]. Here, we present the performances of the gas chemi-resistors based on graphene fabricated through a process specifically developed to lower the growth temperature down to 850 °C. This value is significantly much lower than the 980 °C usually adopted as graphene growth temperature [2,4,5]. The choice to reduce the growth temperature is motivated by the fact that a lower growth temperature can reduce the energy consumption during the graphene growth and facilitate large scale production of these gas sensors. We demonstrate that the sensors performance is not affected by lowering the material growth temperature, thus preserving the above mentioned benefits.

2. Materials and Methods

2.1. Sensors Preparation

The graphene-based gas sensors presented in this study were fabricated on 4" Si (100) wafer covered by thermally grown SiO₂ (90 nm). A thin film of Mo (50 nm) was sputtered from a pure (99.95%) Mo target. Afterwards, dry etching was used to pattern the Mo layer, as described in our previous work [5]. The graphene growth on the patterned Mo catalyst was carried out in an AIXTRON BlackMagic Pro at 850 °C, using Ar/H₂/CH₄ as feedstock at a pressure of 25 mbar. The Mo catalyst was then etched away following the transfer-free process (TFP) we developed [5] and the graphene film laid on the SiO₂. Evaporated Cr/Au (10/100 nm) electrical contacts were defined on the top of graphene film using a lift-off process.

2.2. Sensors Characterization

The devices were electrically characterized by a semi-automatic probe-station with an Agilent 4156C semiconductor parameter analyzer.

Three different tests were performed on the gas sensors in a Gas Sensor Characterization System (GSCS, Kenosistec equipment) setting temperature and RH at 22 °C and 50%, respectively.

2.3. Sensors Test-Protocol Description

The first test, in the following addressed as *Test 1*, consists of a single exposure at 1 ppm of NO₂ 10 min long, preceded and followed by 20 min of baseline and recovery phases, respectively, in N₂ atmosphere.

The second test, *Test 2*, consists of 5 sequential pulses of NO₂ at 1 ppm, similarly to *Test 1*.

Finally, *Test 3* is made of 12 sequential pulses of NO₂ at different concentrations ranging from 1.5 down to 0.12 ppm, each step being 4 min long. The baseline and recovery phases lasted 20 min, respectively. Only the baseline preceding the first step was set 10 min longer than in the other steps in order to further stabilize the devices in the test chamber.

3. Results and Discussion

In Figure 1, the I-V characteristics of the fabricated devices (inset) are showed. Red and black lines are referred to devices based on graphene grown at 850 °C and 980 °C, respectively.

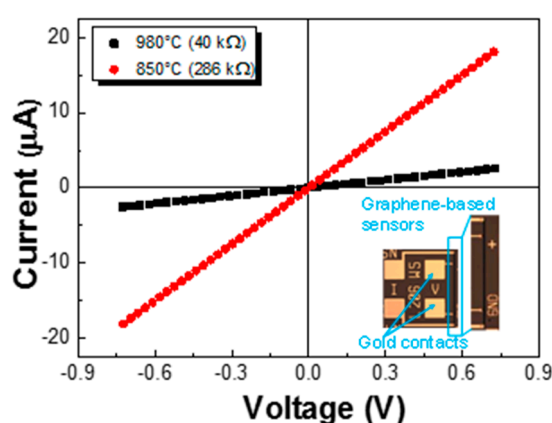


Figure 1. I-V characteristics of the graphene-based resistors reported in the inset.

The linear behavior of the two curves proves that the Ohmic contact was successfully realized between graphene and the Cr/Au contacts. The different resistance value can be ascribed to the differences in the material crystallinity.

Such prepared chemi-resistors were tested upon the abovementioned three different protocols. In Figure 2, the real-time current behaviors of the chemi-resistors upon exposure to a single (Figure 2a) and five sequential pulses of NO₂ (Figure 2b) are showed.

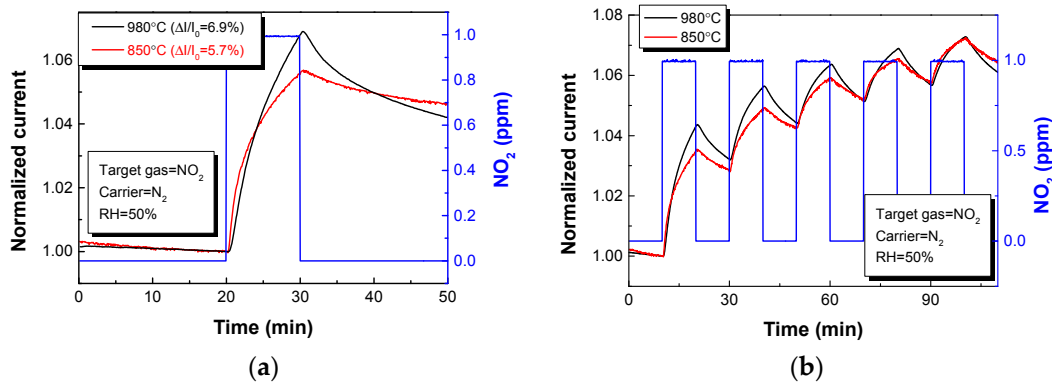


Figure 2. (a) Normalized current of the chemi-resistors upon exposure to 1 ppm of NO₂ under ambient conditions; (b) Real-time current behavior of the chemi-resistors upon exposure to 5 sequential pulses of NO₂ at 1 ppm. In both panels, the current is normalized to the value of the gas inlet during the first pulse. The blue line refers to the NO₂ flow injections. The red and black lines refer to sensors based on graphene grown at 850 °C and 980 °C, respectively.

Figure 2a reports the current variation $\Delta I/I_0$ of the sensors towards *Test 1*, where I_0 and I represent the current values at the inlet and outlet of the NO₂ flow, respectively. For sensors named “850 °C”, $\Delta I/I_0$ was estimated to be roughly equal to 6%. As comparison, $\Delta I/I_0$ for sensor named “980 °C” was around 7%, providing the first indication that the sensors performance is not significantly affected by lowering the temperature of graphene growth.

Figure 2b also attests the substantial equivalence between the two devices behavior, showing the overall same kinetics upon *Test 2*. In Figure 3, this comparison is further addressed. For both sensors, the current recorded during each gas pulse of *Test 2* is compared. The signal is normalized to the value I_0 at the gas inlet of each step. It is worth to note that, in both cases, same trend of the signal and current variation decreasing are noticed. For instance, for both sensors, the difference between the first and second step is about 2%. On the other side, the other steps do not present appreciable differences between the two sensors’ performances.

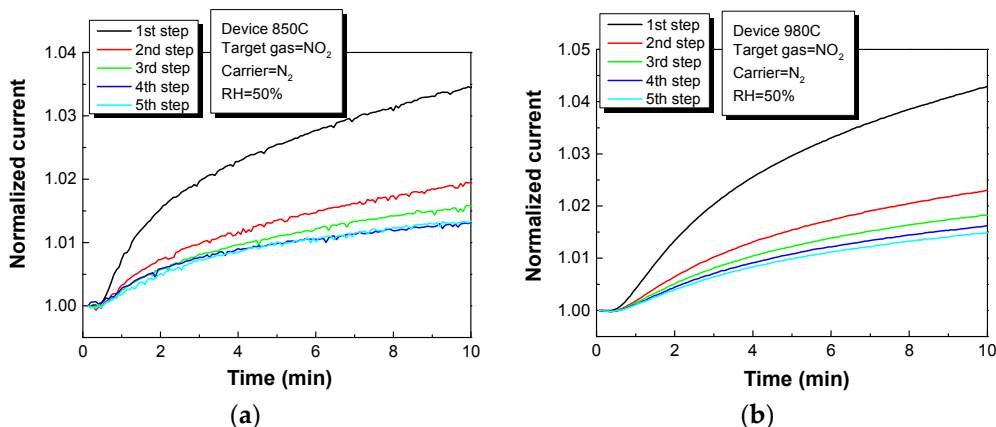


Figure 3. (a) Normalized current signals recorded upon the exposure to the 5 sequential pulses as reported in Figure 2b for device “850 °C”; Plots in panels (b) refer to device “980 °C”.

Finally, the sensors were undertaken to *Test 3* and the results are showed in Figure 4. Black and red lines refer to device “850 °C” and device “980 °C”, respectively. Curves in Figure 4b, extrapolated from Figure 4a, show the plot $\Delta I/I_0$ as function of NO₂ concentration, where I_0 represents the current value at the gas inlet for each gas pulse.

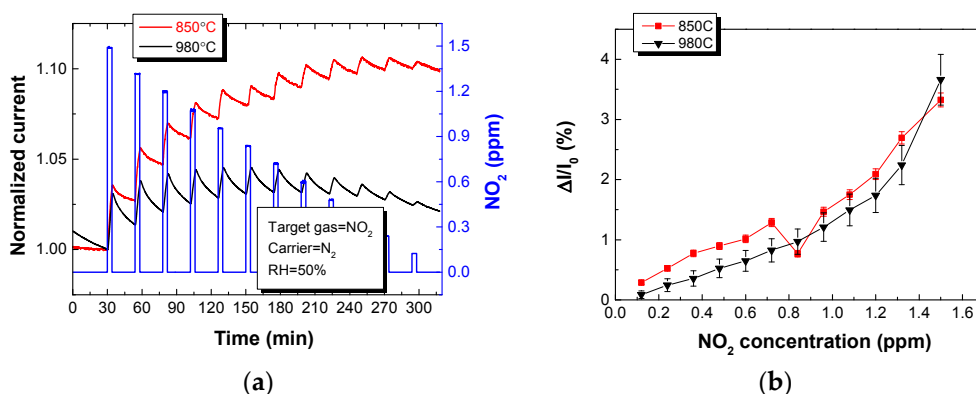


Figure 4. (a) Real-time current behavior of the chemi-resistors upon exposure to 12 sequential pulses of NO₂ at different concentrations ranging from 1.5 down to 0.12 ppm. The signals are normalized at I_0 , representing the current value at the gas inlet during the first pulse; (b) Plots of $\Delta I/I_0$ as function of NO₂ concentration, where I_0 represents the current value at the gas inlet for each gas pulse.

Therefore, within the error bar, Figure 4b definitively discloses the substantial comparability of the findings, although the different growth temperature for the graphene.

4. Conclusions

In this work, we presented gas sensors based on graphene grown by CVD at 850 °C. Such sensors were tested towards NO₂ under environmental conditions, i.e., room temperature and relative humidity set at 50%. The performances were compared with those of devices based on graphene grown at 980 °C, which is usually adopted as growth temperature for such material. The different tests carried out on both sensors definitely uncovered that the sensing behavior is not affected by lowering the growth temperature of graphene. Therefore, these results indicate that energy consumption can be significantly reduced during the large scale production of graphene and graphene-based sensors by CVD technique.

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Conflicts of Interest: The authors declare no conflict of interest.

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