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Graphene-based Schottky device detecting NH₃ at ppm level in environmental conditions

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Abstract

We present a graphene/n-Si Schottky junction for NH₃ detection at level of few tens of parts-per-million (ppm). Graphene was synthesized by Liquid Phase Exfoliation and transferred onto the Si by drop casting. The Schottky barrier characterization towards NH₃ was performed by volt-amperometric measurements in the range 10-200 ppm at bias of -3V. The characterization in the test chamber simulated environmental conditions by Relative Humidity at 50% and temperature at 295 K. Results suggest that the NH₃ induces a barrier height modulation with current variations up to 4% for 200 ppm. In environmental conditions, a spontaneous restoring is observed for the device.

Keywords: graphene; Schottky junction; gas sensing; environmental monitoring

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1. Introduction

Nomenclature

ppm   parts-per-million
LPE   Liquid Phase Exfoliation
RH   Relative Humidity
RT   Room Temperature
C NH_3 concentration
SBH   Schottky Barrier Height

One of the most promising applications for graphene, with its great reactivity upon different substances, is the environmental monitoring of different toxic gases. Up to now, quite a few works on this subject have been produced, based on several transduction principles, mostly the drain current variation in thin film transistors [1] and the change of the conductivity in chemi-resistors [2, 3, 4]. A Schottky graphene/Si junction has been also proposed for detection of liquids and gases [5] where the interaction with the analytes relies on the chemical modulation of both the Schottky Barrier Height (SBH) and the sheet resistance of the graphene film, by reaching a detection of NH_3 in the range of few percent in dry environment. Up to date, no literature data are available on the performances of the graphene-based sensors in environmental conditions. Likely, because of the strong reactivity of graphene to many substances, the selectivity and the reproducibility of the performances is a topic continuously investigated.

On these bases, we report our contribute by a study of a graphene/silicon Schottky junction for NH_3 detection in environment, aimed to investigate the mechanisms involved at standard temperature and humidity conditions.

2. Methodology

We first prepared a basic structure by depositing 250 nm of SiO_2 on a n-type Si wafer ($N_D \approx 5 \cdot 10^{15}$ cm^{-3}); this deposition was masked to leave an area of exposed Si of 4x4 mm^2 as cathode of the junction. A top contact of Cr/Au (30 nm/120 nm) was e-beam evaporated in an annulus shape on the oxide in order to surround the exposed Si. As back contact for the structure, a Ti/Pd/Ag film was realized by e-beam evaporation. The graphene flakes were prepared by Liquid Phase Exfoliation (LPE) using as solvent a mixture of 2-propanol and water in which 2.5 mg/ml of natural powdered graphite (Sigma-Aldrich, product 332461) were dispersed. After a mild sonication of 150 hours, the suspension was centrifuged at 1000 rpm for 45 minutes to separate the thinner flakes. Then, few microlitres of the graphene feed solution were drop-casted on the basic structure, so that the graphene covered simultaneously the top contact and the silicon, insulated between them by the oxide. I-V data were taken by a Keithley 4200 SCS connected to a probe station. The graphene was analyzed by Micro Raman Spectroscopy through a Renishaw inVia Reflex apparatus. All Raman spectra were captured in backscattering configuration (λ=514.5 nm) with a 100x objective on SiO_2/Si substrate [6]. The sensing tests were performed in a Gas Sensor Characterization System (Kenosistec) by keeping Relative Humidity (RH) and temperature at constant values of 50% and 295 K [6].

3. Results and discussion

Raman spectra display the typical profile of LPE graphene. The shape and position of the peaks indicate that the graphite is exfoliated down to less than five layers, as discussed in detail in ref [6]. The electrical characterizations performed on the structure confirmed a rectifying behavior with the formation of a Schottky barrier at the graphene/Si interface. In Fig. 1 the test results of repeated cycles are reported at different NH_3 concentrations (*C*). The variations of the current device due to the ammonia show a good repeatability between two repeated cycles at the same concentration. The device is able to detect 10 ppm of NH_3 in air, corresponding to the minimum tested concentration. Anyway, and more interestingly, the sensing device shows a restore that is reached spontaneously in about 10 min without resorting to annealing or exposure to UV radiation [1, 3, 5]. Starting from the data showed in Fig. 1, we calculated the Fermi level variation ΔE_F induced in the hetero-junction by the NH_3 interaction. For this purpose, the saturation current just before the gas inlet can be expressed as:
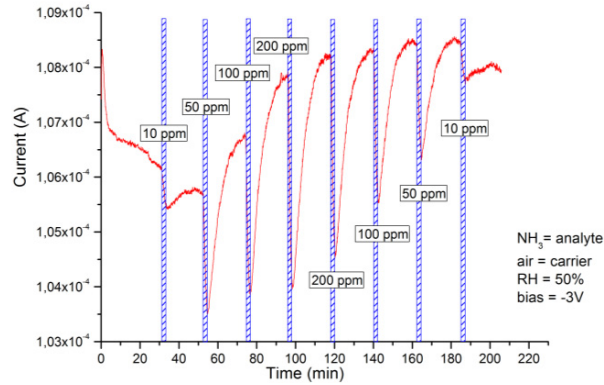
Fig. 1. Current signal after several cycles upon 2 min of exposure to different NH_3 concentrations. The device was reverse biased at 3V. The measurement was carried out in environmental condition (T=295 K and RH=50%) using synthetic air as carrier.

$$I_0 = AA^{**}T^2 \exp\left(-\frac{\phi_{B(-3V)}}{kT}\right)\left[\exp\left(\frac{qV}{nkT}\right)-1\right] \tag{1}$$

where T is the absolute temperature, A the effective area of the junction, A** the effective Richardson's constant for n-Si substrate, k the Boltzmann constant, V=-3V and n the ideality factor and finally, $\phi_{B(-3V)}$ is the SBH at -3V, which depends on bias because of the electrical tunability of the Fermi level in graphene [8]. When the diode is exposed towards the NH_3, we measure a minimum current

$$I_{min} = AA^{**}T^2 \exp\left(-\frac{\phi_{B(-3V)}-\Delta\phi_{NH_3}}{kT}\right)\left[\exp\left(\frac{qV}{nkT}\right)-1\right] \tag{2}$$

where $\Delta\phi_{NH_3}$ is the SBH variation due to the ammonia exposure amount. From equations (1)-(2), ΔE_F is then given by:

$$\Delta E_F = \Delta\phi_{NH_3} = kT \ln\left(\frac{I_{min}}{I_0}\right) \tag{3}$$

Because our analysis is based on reverse bias only, the contribution from the series resistance is negligible. In Tab. 1 both variations of the current signal and ΔE_F for different analyte concentrations are reported.

Table 1: Current signals and Fermi level shift vs NH_3 concentration at RH=50%.

NH_3 concentration (ppm)	I_0 (μA)	I_{min} (μA)	ΔE_F (eV)
10	106.2	105.4	-1.9E-4
50	105.7	103.5	-5.3E-4
100	106.7	103.8	-7.1E-4
200	107.8	104.0	-9.1E-4

Fig. 2 reports $\Delta\phi_{NH_3}$ *vs.* NH_3 concentration, implicitly assuming that $\Delta\phi_{NH_3} = \Delta\phi_{NH_3}$ (*C*). This dependence is currently still under investigation because of the adsorption mechanisms regulating the doping in the device. Based

on previous works [8, 9, 10] a preliminary analysis, not reported here for brevity, leads to suppose the dependence on C as $\Delta\phi_{NH3} \propto C^{0.5}$. In Fig. 2, the plot represents the empirical fit of the data $\Delta\phi_{NH3} = a\,C^b$.
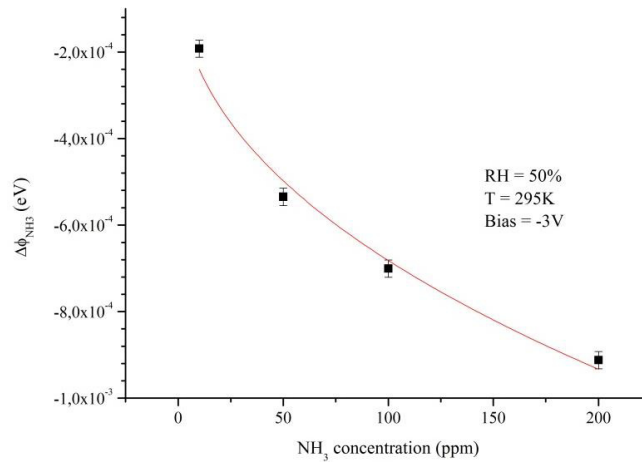

Fig. 2. Curve reporting the SBH variations vs NH$_3$ concentration in the range 10-200 ppm (T=295 K and RH=50%).

We obtain, for the empirical parameters, the values: $a = -8 \pm 2 \times 10^{-5}$ eV ppm$^{-1/2}$ and $b = 0.45 \pm 0.05$ respectively. To confirm the theory subtended, other sensing tests are ongoing by varying the analyte type and RH.

4. Conclusions

The diode current at fixed values in reverse bias was investigated for several concentrations of NH$_3$ ranging between 10 to 200 ppm. Preliminary measurements suggest that the signal I_{min}/I_0 is related to the concentration of analyte the device is exposed to. Further investigations towards other analytes of interest in the field of environmental monitoring are ongoing. The device shows a very good recovery which is reached without resorting to techniques such as thermal annealing or exposure to UV radiation, contrarily from what is generally reported in the literature for solid state sensors which work at RT.

5. References

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