Highly Sensitive NH₃ Sensors Using CVD and Epitaxial Graphene Functionalised with Vanadium(V) Oxide: A Comparative Study [†]

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† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Abstract: Exceptionally sensitive and selective graphene-based chemiresistive gas sensors were produced as a result of graphene functionalisation with a sub-nanometer V_2O_5 layer by using the method of pulsed laser deposition. Two different types of graphene were used—epitaxial graphene on SiC and CVD graphene on Si/SiO₂—and both showed remarkable enhancement of sensing properties in terms of response and recovery speed, response magnitude and selectiveness towards NH₃ gas. The epitaxial graphene-based sensor was demonstrating the highest relative response towards ammonia amounting to 80% for 0.1 ppm NH₃.

1. Introduction

Since its discovery, graphene as a monolayer-thick (semi)conducting material was investigated as a gas sensing system, with great potential for miniaturization, low-power operation and cheap production [1]. However, realization of practical sensing systems functioning in real atmosphere with the high concentration of oxygen and water vapor is still challenging. Enhancement of sensing properties of graphene is possible by promoting gas adsorption through introducing defects, atomic dopants, or by functionalisation with nanoparticles [2]. A pulsed laser deposition of a sub-nanometer thick layer of catalytically active V_2O_5 gives CVD graphene remarkable sensitivity and selectivity towards ammonia gas [3]. Even greater improvement would be expected in the case of epitaxial graphene, because of its higher sensitivity to chemical doping as a result of its lower intrinsic doping level [4].

In the current work, the chemical vapour deposited graphene on Si/SiO₂ (Si/SiO₂/CVDG), and the epitaxial graphene grown on SiC (SiC/EG) were functionalised by laser deposited ultra-thin (0.6 nm) V_2O_5 layer. The effect of PLD process on graphene defect creation was investigated by Raman spectroscopy. The NH₃ gas sensing properties are compared for pristine and V_2O_5 deposited graphenes. Responses of both types of graphene sensors to other polluting gases NO₂, CO, SO₂ and O₃ were researched to test the selectivity.

2. Materials and Methods

Chemical vapour deposited graphene was grown on a commercial 25 μm thick polycrystalline copper foil in a home-built CVD reactor. The grown graphene film was transferred onto Si/SiO_2 substrate carrying Au (60 nm) electrodes deposited through a shadow mask by magnetron sputtering. The graphene growth and transfer processes were executed as described earlier [3]. Epitaxial graphene (EG) was grown by sublimation method on Si-terminated 4H–SiC (0001) substrates at 2000 °C in argon gas at 1 bar [5]. Au (200 nm) contact pads were made by evaporation on top of SiC/EG substrate. In the PLD process, a ceramic V_2O_5 target was ablated with a KrF excimer laser at wavelength 248 nm and laser pulse energy density of 5.0 J/cm^2, in the presence of 5×10^{-2} mbar of O_2. The total of 120 laser pulses with a repetition rate of 5 Hz was used for V_2O_5 layer deposition. Sensor substrates were kept at the room temperature during deposition.

Gas sensitivity was measured the room temperature in a 7 cm^3 stainless steel sample chamber, equipped with a gas mixing system [6]. The voltage applied to the electrodes was 100 mV. In the experiments with UV light excitation, the 365 nm light intensity on the sample was ~15 mW/cm^2.

3. Results and Discussion

According to the analysis of vanadium valence state by X-ray photoelectron spectroscopy (XPS) and a mass thickness measurement by X-ray fluorescence (XRF), the material deposited on graphene is predominately in the highest stable oxidation state of vanadium, V_2O_5, and has an average thickness of ~0.6 nm [3].

As indicated by the Raman spectrum (Figure 1), the defectiveness of CVD graphene increased drastically as a result of PLD, which is an expected result of high energy atomic bombardment with PLD plasma species. The rise of defectiveness by PLD is evident from the emergence of prominent defect-related D and D′ bands, and a height decrease of G and 2D bands at the same time. By contrary, for EG on SiC substrate the typical Raman peaks indicate that graphene remained intact after identical PLD treatment. This implies a much larger resilience against the defect creation, probably due to much tighter graphene-to-support contact in case of EG on SiC. This interpretation is also supported by the fact that the electrical conductivity of SiC/EG sample did not change after the PLD of V_2O_5, whereas the conductivity of CVD graphene sample dropped substantially.
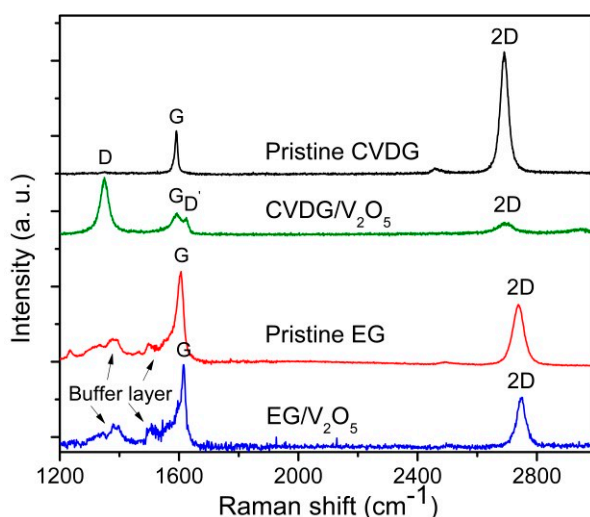

Figure 1. Typical Raman spectra of CVD and epitaxial graphene in the sensor devices, recorded between the electrodes before and after the laser deposition of V_2O_5: strong defect-related peaks D and D′ after deposition on CVDG did not appear noticeably in case of SiC/EG.

Compared to unmodified graphene, large improvement of sensor response to the reducing NH_3 gas was achieved for both types of graphene sensors (Figure 2). The SiC/EG showed by an order of magnitude larger response, as compared to CVDG sensor. For instance, the relative response to 100

ppm NH_3 was 295% and 31% in case of EG and CVDG sensors, respectively. The conductivity of different types of graphene sensors changes in opposite direction after introducing NH_3, due to different types of majority charge carriers—electrons in $Si/SiO_2/CVDG$ and holes in SiC/EG.
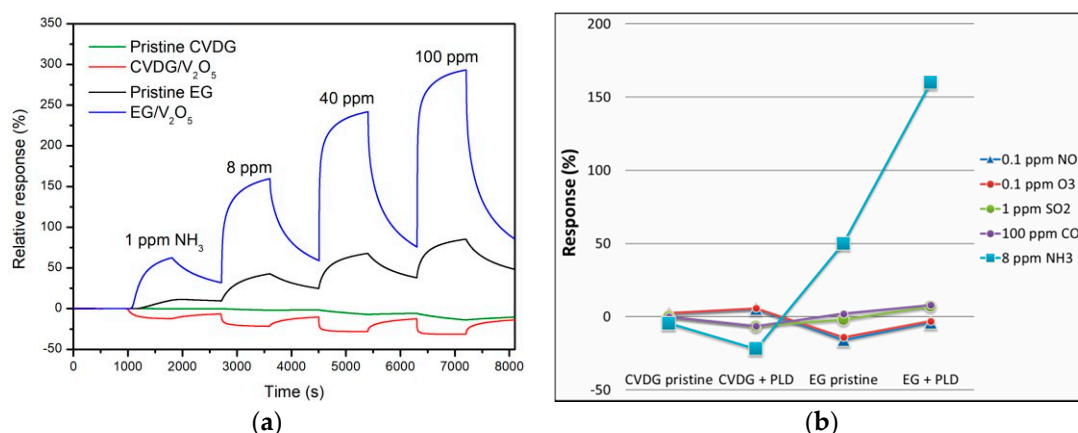

Figure 2. Influence of graphene functionalisation with V_2O_5 on gas sensitivity and selectivity: (**a**) Electric conduction response of CVD graphene on Si/SiO_2 and EG on SiC to different NH_3 concentrations at room temperature. Results for pristine graphenes are shown as a reference. Permanent UV light was on during the measurements. Relative humidity was 20%. All time intervals of gas exposure and recovery are 900 s; (**b**) Sensor response amplitudes to different polluting gases of CVD graphene (CVDG) and epitaxial graphene (EG) sensors with and without laser deposited V_2O_5 layer.

In addition, considerably faster characteristic response times were measured on both types of sensors after deposition (by 4 to 6 times). Again, the improvement of the response and recovery speed was more drastic for the SiC/EG sensor. Enhancement of gas response can be caused by increased density of energetically favourable adsorption sites or/and increased charge transfer from NH_3 adsorbate molecules [4]. Strong adsorption ability of NH_3 on V_2O_5 and possible redox reactions on the surface of V_2O_5 are well known [7]. Although perfect graphene is relatively inert with respect to chemisorption, owing to low concentration of dangling bonds and lack of charged atoms on the surface [2], the as-made, or pristine graphene almost always shows considerable gas sensitivity to NO_2 and NH_3, in conjunction with extremely slow sensor recovery at RT [1,2,8]. High adsorption energy binding sites may exist in freshly produced graphene, such as uncontrollably introduced defects or dopant atoms in the graphene lattice. In the course of functionalisation a high number of point defects is formed by bombardment with high-energy atoms of PLD plasma. The induced defects are further modified through the adding of functionalising oxide material [3,9].

The recovery kinetics and the dependence of sensor response magnitudes on NH_3 concentration are in accordance with Langmuir type two-site adsorption model [10]:

$$S_x = \frac{G_x - G_0}{G_0} = \alpha_1 \frac{xb_1}{1 + xb_1} + \alpha_2 \frac{xb_2}{1 + xb_2}, \tag{1}$$

where b_1 and b_2 are affinity constants, α_1 and α_2 are transduction coefficients.

Fitting the data with the model resulted in two important consequences regarding functionalised graphene sensors:

1. Adsorption sites with comparable affinity constants b_1 and b_2 on both types of graphene indicate the similar effect of deposited V_2O_5 nanophase on the surface.
2. Both transduction coefficients α_1 and α_2 are much smaller in case of CVD graphene sensor, which means less influence of gas adsorption on relative conductivity, and hence, lower relative gas response of the CVD graphene sensor. Taking into account that the gas adsorption mainly modifies the charge carrier concentration rather than mobility [1], the substantially larger

response of EG sensor is probably arising from lower initial carrier doping of EG as compared to free electron concentration in CVD graphene.

The selectivity with respect to NH_3 of both CVDG and EG sensors increases after the PLD of V_2O_5, when compared to the response to several other polluting gases. For instance, in case of EG, the response to NH_3 increases significantly by functionalisation, and at the same time, the response to NO_2 gas is reduced, thus improving the selectivity. The functionalisation with V_2O_5 slightly increases the response to CO and SO_2 gases for both types of sensors, both gases being reducing. As expected from the strongly oxidizing properties, reactions to O_3 and NO_2 gases are much alike.

4. Conclusions

CVD-grown graphene (Si/SiO_2/CVDG) and the epitaxial graphene grown on SiC (SiC/EG) were functionalised by laser deposited ultra-thin V_2O_5 layer (0.6 nm). Compared to pristine graphene sensors, large and selective enhancement of sensor response to the reducing NH_3 gas was achieved for both types of graphenes. The effect of metal oxide modifier was more remarkable for EG which showed, as compared to similarly functionalised CVDG sensor, by an order of magnitude larger response (295% vs. 31% for 100 ppm NH_3). The recovery kinetics and dependence on NH_3 concentration are in accordance with Langmuir type two-site adsorption model. The results imply the presence of similar adsorption sites on both types of materials, indicating a similar role of deposited V_2O_5 nanophase on the surface. The substantially larger response of EG sensor is probably the result of the lower initial carrier doping in EG.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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