Research Article

Plasma-Treated CVD Graphene Gas Sensor Performance in Environmental Condition: The Role of Defects on Sensitivity

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In this work, a low-cost resistive gas sensor based on graphene grown by CVD was fabricated and its sensitivity was studied in terms of defect density. CVD graphene was transferred using Polyurethane as sacrifice layer with low contamination and defect-free results. An atmospheric plasma etching system was used to homogeneously induce defects on the sensor’s active area, as investigated through Raman spectroscopy. Device sensing properties were significantly enhanced for greater defect density for both NH₃ and NO₂. The modified sensors were submitted to different concentrations of both target gas to assess detection limits and overall behavior. It was revealed that defective CVD graphene devices possess sensitivity up to ppm range with linear dependence in the range of values measured. The fabricated sensors presented little to no signal degradation after months of atmospheric exposure.

1. Introduction

Since graphene first gas detection investigation published in 2007 [1], numerous efforts have been made towards its extended application in the area [2, 3]. 2D materials, such as graphite, have attracted enormous attention given that they usually show different properties from their three-dimensional counterparts. Since most chemical sensors are based in the interaction between an active surface and a target gas, it is straightforward to understand that graphene’s extremely high surface area/volume ratio makes it ideal for its use in gas sensing devices.

In this regard, the need to growth and isolate large-area graphene on suitable substrates for electronic applications becomes apparent. Chemical Vapor Deposition has been used for many years as a suitable option for the growth of polycrystalline graphene, with a highly reproducible process and sufficient quality for most requirements [4, 5]. CVD-grown graphene natural defects are also somewhat desired, as defects and irregularities are well-known adsorption sites in most solid state gas sensors in use today [6, 7].

On the other hand, too many defects in the graphene surface may promote adsorption but also have a substantial effect in the film electrical conductivity. A typical example of this is seen in graphene oxide films: as deposited, they present an enormous amount of adsorption sites given by its sheet irregular agglomeration, which conversely causes high resistance values and poor effective contact [8].

Numerous ab initio studies have found that defects on graphene enhance its sensing properties (DFTs) and experimental works have confirmed this behavior [9–11]. It has been shown in the work by Salehi-Khojin et al. [9] that defective graphene is not only more sensitive than pristine but also that a combination of different types of defects is desired. Lastly, it has also been reported by Rigoni et al. [12] that UV radiation may increase the sensor’s response by introducing defects and aiding desorption during the recovery process. Despite all that, the mechanism of response of the graphene properties to the variation of defect density for
CVD graphene in an atmospheric environment is yet to be fully understood.

In this work, we studied graphene sensing properties upon successive increases in uniformly distributed defects. To obtain this homogeneously defect density, atmospheric plasma etching was used. NO$_2$ and NH$_3$ were chosen as target gases. The two analytes studied in this work are among the most treated for research in the field, because these toxic gases have been demonstrated to have significant negative impacts on health and the environment. However, the dangerousness towards analytes mostly depends on some parameters related to the exposure time. To this aim, different definitions of limit values and accordingly thresholds can be considered, taking into account different endpoints or averaging times. Independently from the various definitions and the countries taken into account, the analyte concentration ranges to not exceed are quite stringent. Indeed, the general aim of research and technology is to find routes to make possible the detection and measurement of gases at levels of ppm.

Raman spectroscopy was used to monitor defect density and distribution [13]. It was shown that defective sensors presented enhanced response to the same concentration of both target gases. A higher sensitivity was observed for NO$_2$, which may be explained by the water adsorption on the sensor surface as seen in [12]. It was also revealed that

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**Figure 1:** SEM images of CVD graphene as grown on Cu (a) and after transferred onto SiO$_2$/Si (b). (c-e) Details of the interdigitated chemiresistor; (d) I/V graphic. Distance between fingers is 60 microns.
the as-fabricated defective sensors present linear response variation with concentration for both gases, with detection limits ranging to the few ppm scale.

2. Experimental Details

All sensors used monolayer graphene grown on copper foils by Low Pressure Chemical Vapor Deposition (LPCVD), using a \( H_2 \) annealing flux and methane gas as precursor at 1050°C and 500 mTorr of total pressure. All films were transferred on to \( SiO_2/Si \) substrates using a modified wet-transfer method using Polyurethane (PU) as sacrificial layer and Tetrahydrofuran (THF) as solvent. PU thin films were spin-coated on the graphene surface, and the copper was subsequently etched using an iron chloride (\( FeCl_3 \)) solution for 1 hour. After transferring graphene on to the silicon oxide substrate, PU film was removed by rinsing in THF for 3 hours. Scanning electron microscopy (SEM) images were obtained using a FEG-SEM model JSM-6701F from JEOL.

SEM images of the as-grown graphene sheets on copper and after the transfer process onto \( SiO_2/Si \) as described are shown in Figures 1(a) and 1(b), respectively.

Defects were introduced by atmospheric plasma etching through a Harrick plasma model PDC-32G. The amount of defects was adjusted depending on period of exposure, going from 5, 10, 20, and up to 30 seconds. Each sample was then submitted to Raman spectroscopy to quantify defect density,
using a NTEGRA spectrometer from NT-MDT with emission wavelength of 473 nm.

Each sample was then mounted onto the sample holder and placed inside a cylindrical stainless steel chamber (1.7 liters of volume) with a small diaphragm pump installed for vacuum. Commercial traceable standard mixtures supplied by Linde Industrial Gases of 100 ppm of NH₃ and 150 ppm of NO₂, both on a nitrogen base, were used to test the sensor’s performance. All measures were made at room temperature (295 K) and 50% relative humidity, and total pressure inside the chamber was adjusted to 700 torr. MKS Instruments mass flow controllers were used for gas release (NH₃ and NO₂ mixtures, 99.99% pure N₂ also from Linde or air).

Initially, the samples were placed in vacuum for a period of 3 hours in which a resistance baseline value was attained, with less than a 0.5% variation observed in 10 minutes. Then, an air flux was released and the baseline readjusts to the new conditions in approximately one hour. After that, the air flux was substituted by a controlled moisture flux, keeping pressure constant throughout the measurement. Typical exposure time to both target gases was set to 10 minutes. Then, after 3 hours in which a resistance baseline value was attained, both on a nitrogen base, were used to test the sensor’s performance.

Figure 3: Sensor response to NO₂ and NH₃ as a function of the time of plasma treatment.

3. Results and Discussion

As previously discussed, defects were generated by atmospheric plasma as appreciated by Raman spectroscopy shown in Figure 2(a). The 2D band (∼2700 cm⁻¹) and G band (∼1580 cm⁻¹) intensity ratio (I₂D/I₁G), a well-known indicator of monolayer graphene, decreases with higher plasma exposure times as expected, while the D band (∼1360 cm⁻¹) vs. G band intensity ratio (I_D/I_G) rises, as shown in Figure 2(b). This latter indicator usually is mainly associated with the presence of defects. It has been also established that high D peak intensity in conjunction with the appearance of a D’ band (∼1620 cm⁻¹), as observed, further signals defects in the graphene structure [13].

Even more, it has been reported that the value of intensity ratio between the D and the D’ bands (I_D/I_D’) indicates the prevalence of different types of defects in a graphene sample, (∼13) for sp² defects and (∼7) for vacancy-like defects [14]. In this regard, it may be inferred from the measurements that initial bombardment created numerous sp³-related defects, but eventually the D’ band higher intensities for higher exposure periods denotes vacancy-dominated samples.

Raman maps showed that plasma-created defects were homogeneously distributed, as shown through Raman maps for 10 seconds (Figure 2(c)) and 30 seconds (Figure 2(d)) of plasma exposure. Local Raman spectrum variation, observed mainly in the form of cracks and wrinkles in the film, was all due to growth and transfer-related processes. Image histograms of (I_D/I_G) ratio indicates the presence of highly uniform surfaces, more so for higher exposure periods.

The values corresponding to G and 2D bands presented a slight blue shift as the exposure time increased, caused mainly because of the broadening of the peaks caused by the induced defects. Both Raman maps presented in Figure 2 average shift values (in the whole map) for the G and 2D peaks were 1589.4 cm⁻¹ and 2709.1 cm⁻¹ for the 10-second plasma exposure and 1592.5 cm⁻¹ and 2711.4 cm⁻¹ for the 30-second exposure. Both G and 2D shifts are an indicator of the p-type behavior the sensors showed.

In Figure 3, we resume response of the sensor to exposure to different gases as a function of the time of plasma treatment. It is clear that the response increases upon the increase of the duration of the processing. The response of the sensor is illustrated also in Figures 4(a) and 4(b). The response changes as a function of plasma exposure as seen in Figures 4(a) and 4(b). In Figures 4(c) and 4(d), it was shown for plasma processing time of 30 minutes the recovery behavior of the sensor. Total recovery was not achieved, signaling that full desorption might require further treatment.
However, it was not identified a clear relation between recovery rates and plasma exposure time.

It was also investigated the sensor performance when submitted to different concentrations of the target gases. For this, an additional pure nitrogen flux was introduced to the previous target gas mixtures in-flux, in such way that the total flux released into the chamber remained constant. When exposed to different concentrations of NH$_3$ and NO$_2$, as shown in Figures 5(a) and 5(b), the sensors registered clear signals up into the range of tens of ppm. It was also found that the response is directly proportional to the concentration of the target gas as shown in Figure 5(c). From the linear regression curves of both series, it may be estimated that below 2 ppm for NH$_3$ and 18 ppm of NO$_2$ the response will no longer be reliable.

### 4. Summary and Conclusions

In summary, monolayer CVD-grown graphene sheets were transferred to SiO2/Si substrates using PU as sacrifice layer in the transfer process. A chemiresistor was fabricated on top of the as-transferred graphene layer, and homogeneous defects were then induced by plasma. The density and type of defects produced were investigated as a vital factor in the sensor response. Raman spectroscopy proved uniformly distributed defects in the graphene sheet after plasma exposure. Device sensing properties were highly influenced by the defect density for both NO$_2$ and NH$_3$ gases. In general, all devices showed greater response to NO$_2$, which may be explained by the predominant number of vacancy-type defects caused by plasma etching. All devices showed...
almost complete desorption when exposed to air and a response was recorded up to tens of ppm range for both gases. The as-created chemiresistors showed low resistance and an enhanced response to both target gases, all of that while not showing any signal degradation after atmospheric exposure.

To be competitive with commercial sensor technologies, graphene-based sensors must be mass producible at low cost. With the recent improvement of the CVD synthesis method [5], the issue of large-scale graphene production is apparently about to be overcome. In our devices, another bottleneck which is the need of high-temperature desorption for gases of \( \text{NO}_2 \) and \( \text{NH}_3 \) on graphene surfaces is surmount, as is clear from Figures 4 and 5. Concluding, the increase in sensor sensitivity is the result of simple plasma treatment using air as the active gas, clearly indicating that this device is on the route to be commercially competitive.

**Data Availability**

All the data used to support the findings of this study are available from the corresponding author upon request.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.
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