Iron Oxide Nanoparticle Decorated Graphene for Ultra-Sensitive Detection of Volatile Organic Compounds [†]

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Abstract: It has been found that two-dimensional materials, such as graphene, can be used as remarkable gas detection platforms as even minimal chemical interactions can lead to distinct changes in electrical conductivity. In this work, epitaxially grown graphene was decorated with iron oxide nanoparticles for sensor performance tuning. This hybrid surface was used as a sensing layer to detect formaldehyde and benzene at concentrations of relevance in air quality monitoring (low parts per billion). Moreover, the time constants could be drastically reduced using a derivative sensor signal readout, allowing detection at the sampling rates desired for air quality monitoring applications.

Keywords: epitaxial graphene; metal oxide nanoparticle; gas sensor; volatile organic compounds; benzene; formaldehyde; derivative sensor signal

1. Introduction

Several toxic air pollutants in more than 80% of the urban areas where air pollution is, according to the World Health Organization (WHO), monitored exceeds the WHO recommended safe exposure levels. Poor air quality has been associated with several negative health aspects ranging from less severe conditions such as skin and eye irritation, to more acute respiratory problems, cancer, or death. Air pollution has been estimated to cause 4.3 million annual deaths and to financially burden the European region by about 1.6 trillion US dollars per year [1,2].

Air quality monitoring (AQM) and control using extremely sensitive sensors is crucial from the viewpoint of preventing further deaths and diseases correlated with toxic air substances. However, commercial sensors/instruments available today are either large, expensive, and complex or small but limited by poor selectivity, sensitivity, and a slow sampling rate [3]. In addition, there are no commercially available sensors with sufficient sensitivity to monitor several carcinogenic volatile

organic compounds (VOCs), such as formaldehyde and benzene, at levels of relevance to human health.

Using the unique properties of graphene as a transducer allows fabrication of sensor devices that can be used for gas detection where low concentrations can be detected, including air quality control for human health. Besides a high sensitivity, also interaction with specific target analytes and a good selectivity must be addressed to get a useful sensor device. It has already been shown that decoration of the graphene surface with metal/oxide nanoparticles can lead to a higher sensitivity and selectivity towards certain gases, e.g., nitrogen dioxide, benzene and formaldehyde [4,5]. Using a "soft" decoration approach, the surface chemistry of the sensing layer could be modified without changing the transducer's electronic properties. So far, these sensors were able to detect the mentioned gases down to tens of parts per billion (ppb), but not reliably lower. We demonstrate how it is possible to detect even single ppb concentrations and we further introduce a data evaluation approach allowing fast response times to meet the criteria for AQM.

2. Materials and Methods

2.1. Sensing Layer Preparation

The graphene was grown epitaxially on silicon carbide (SiC) through a sublimation process were an on-axis, semi-insulating (0001) 4H-SiC substrate is used for the formation of graphene in Ar at a temperature of 2000 °C and at a pressure of 1 bar [6]. The method allows highly homogenous growth of monolayer graphene and requires no further transfer to another insulator. Hollow cathode pulsed plasma sputtering [7] was used to functionalize the graphene surface with iron oxide (Fe_3O_4) nanoparticles.

2.2. Characterization Techniques

Before and after the deposition of nanoparticles, a series of characterization measurements were conducted to see if any damage of the graphene surface occurred during the deposition. Atomic Force Microscopy (AFM) (Quadrexed Dimension 3100) with a Nanoscope IVa controller was used in tapping mode to obtain topography images of the sensing layers. The measurements were performed using Si tips (PPP-NCHR-50 from Nanosensors) with a tip radius of curvature <7 nm. A micro Raman setup was used to perform Raman spectroscopy and reflectance measurements. A CCD camera coupled to a monochromator (HR460) was used along with a 100× magnification objective which was excited at 532 nm using a solid-state laser with a power of 17 mW focused to a spot with diameter ~0.9 μm on the sample, and a system spectral resolution of approximately 5 cm^{-1}. The Raman spectra of Si-face graphene were obtained by subtracting a reference Raman spectrum of 4H-SiC (0001). X-ray photoelectron spectroscopy (XPS) studies using a Microlab 310-F spectrometer were performed to investigate possible alterations made to the sample after deposition of nanoparticles and to establish if Fe_3O_4 was present on the surface.

2.3. Sensor Device Fabrication

As a first step, Ti/Au (2/200 nm) contact pads were thermally evaporated onto the EG/SiC before functionalization. The contacts have a size of 1 mm × 1 mm with a distance of 1 mm in between them. The sensor chip and a Pt-100 resistance thermometer were glued (Aremco Ceramabond 571) onto a ceramic heater (Heraeus Sensor-Nite GmbH, Kleinostheim, Germany) to enable a controlled temperature loop and welded to a 16 pin TO8 header. This device was mounted on top of a TO8-socket and connected to its pins using gold-wire bonding and silver glue (Epotek E3081). The final sensor is placed in a flow chamber connected to a gas mixing setup. A Keithley 2601B SourceMeter in two-wire mode is used to measure the resistance between the contacts during gas exposure. The total gas flow was held constant at 100 mL/min and a dry mixture of 80% N_2 and 20% O_2 was used as purging and carrier gas.

3. Results and Discussion

3.1. Morphological and Structural Characterization

Figure 1 shows AFM graphs of the graphene sensor surface before (a) and after (b) the decoration with Fe_3O_4 nanoparticles. Neglecting the characteristic steps corresponding to the SiC step bunching，the as-grown graphene surface in Figure 1a shows almost no roughness. The particle coverage is about 60% and single particles have an average diameter of about 70 nm. Raman spectroscopy confirms structural integrity of the graphene surface also after the decoration [5]. XPS shows additionally to the integrity of graphene the presence of iron oxide on top of the sensor surface (not shown here).
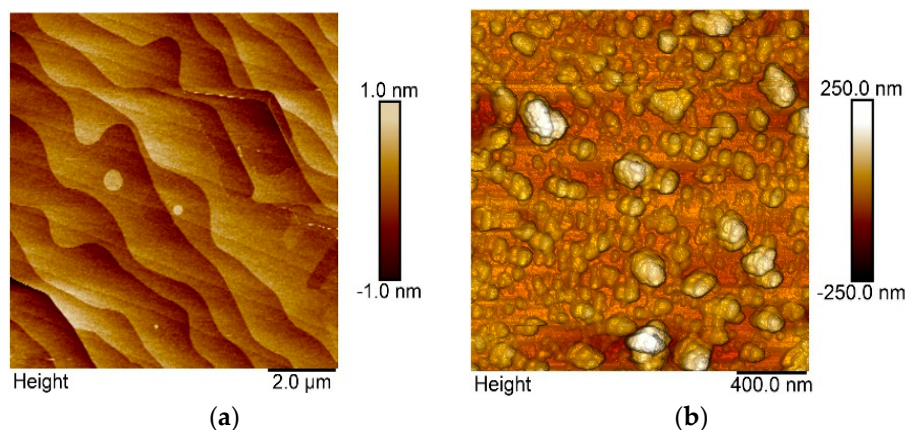

(**a**)   (**b**)

Figure 1. AFM image of the graphene sensor surface before (**a**) and after (**b**) decoration with iron oxide nanoparticles.

3.2. Gas Measurements

After the successful decoration of the graphene surface with Fe_3O_4 nanoparticles, gas measurements were performed. Figure 2a shows how the resistance of the sensor changes with the exposure towards formaldehyde. The sensor was exposed towards formaldehyde and benzene at 150 °C operating temperature in a dry background using concentrations ranging from 5 parts per million (ppm) to 1 ppb. It has already been shown in an earlier work [5] that Fe_3O_4 nanoparticle decorated graphene sensors can be used for formaldehyde and benzene detection, but not over such a large range and down to a single ppb. The response is defined as $\frac{R - R_0}{R_0}$, where R is the saturate resistance signal and R_0 corresponds to the baseline resistance before the gas exposure. The relative response for different concentrations of benzene and formaldehyde is shown in Figure 2b. A distinct response for both gases over the whole range can clearly be observed. Moreover, the safety limit for formaldehyde (~80 ppb) can easily be reached and also benzene (no safety level reported) can be quantitatively measured down to a single ppb. The relative responses towards 1 ppb formaldehyde and benzene are about 0.04% and 0.02%, respectively.

Besides a very good sensitivity, also time constants of these measurements need to be addressed. For an application in indoor air monitoring, the time constants for the sensor should be in the range of half a minute to several minutes, depending on the application. However, as shown in Figure 2a, even an exposure towards the gas over 30 min does not lead to a saturated sensor response. Using the time it takes for the first order time derivative of the sensor signal to reach its maximum for each exposure instead, the time constant can be decreased down to around 50 s. This is exemplarily shown for the first two exposures in the inset in Figure 2a.
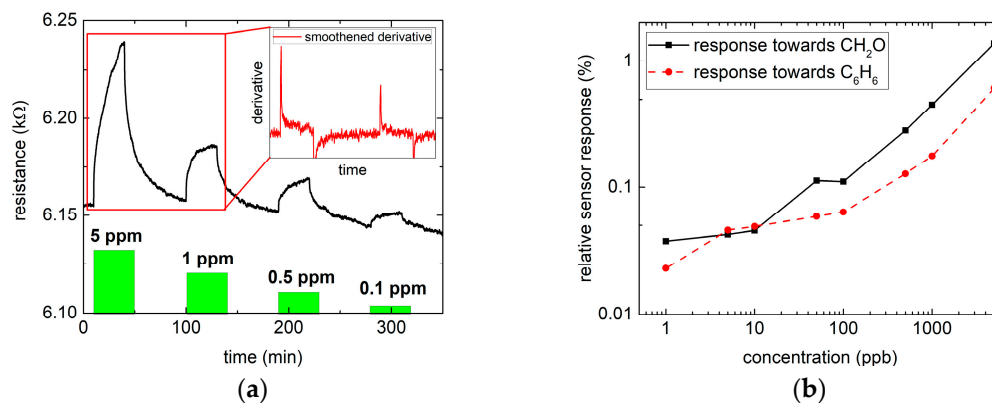
Figure 2. (**a**) Sensor behavior exemplarily shown for the first four exposures (5 ppm–0.1 ppm) towards formaldehyde at 150 °C in dry air with the smoothened derivative signal as inset and (**b**) relative **s**ensor response towards different concentrations of formaldehyde and benzene.

4. Conclusions

Benzene and Formaldehyde sensing properties were investigated using epitaxially grown graphene on silicon carbide decorated with Fe_3O_4 nanoparticles. We could verify the decoration and the integrity of the graphene surface using AFM, Raman spectroscopy and XPS. With this sensor platform, concentrations down to a single ppb of toxic VOCs could be quantitatively measured, which makes it very promising for air quality monitoring. Moreover, the derivative signal readout decreases the time constants down to a speed that is suitable for AQM.

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

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