A Platform for Extremely Sensitive Gas Sensing: 2D Materials on Silicon Carbide

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ABSTRACT

2D materials offer a unique platform for sensing with extreme sensitivity, since minimal chemical interactions cause noticeable changes in the electronic state. An area where this is particularly interesting is environmental monitoring of gases that are hazardous at trace levels. In this study, SiC is used as a base for epitaxial growth of high quality, uniform graphene, and for templated growth of atomically thin layers of platinum, with potential benefits in terms of the ability to operate at higher temperature and to serve as a more robust template for functionalization compared to graphene. Functionalization with nanoparticles allows tuning the sensitivity to specific molecules without damaging the 2D sensor transducer. With this platform we demonstrate detection of nitrogen dioxide, formaldehyde, and benzene at trace concentrations. This, combined with smart sensor signal evaluation allowing fast response times, could allow real-time monitoring of these toxic pollutants at concentrations of relevance to air quality monitoring.

Keywords: graphene gas sensor, 2D metal, benzene, formaldehyde, nitrogen dioxide

1 INTRODUCTION

2D materials, like graphene, offer a unique platform for sensing where extremely high sensitivity is a priority, since even minimal chemical interactions can cause noticeable changes in the electronic state [1], which can be used for sensor readout. Graphene has been extensively studied for gas sensing applications, showing good functionality as a highly sensitive transducer material for sensors [2]. The sensitivity of graphene comes from its unique properties, such as every atom being available for interaction with adsorbing molecules; the high carrier mobility (which often scales with sensitivity); the low density of states near the Dirac point, meaning that minimal charge transfer yields significant change in the electronic state; high electronic conductivity even when very few charge carriers are present [3]; inherently few crystal defects which leads to low Johnson [4] and thermal switching noise [5], in turn leading to high signal to noise ratio.

To fully exploit graphene as an ultra-sensitive transducer, uniform, 'defect-free' material is a key issue. To that end, growth of epitaxial graphene (EG) on SiC can produce uniform continuous graphene over an entire wafer [6] with control over the layer thickness, allowing device reproducibility. Growth on insulating SiC substrates means that transfer to another insulator is not required, and EG/SiC is readily compatible with standard device processing.

Our studies show that material uniformity is a key parameter for device reproducibility in 2D materials, e.g. we have found that monolayer graphene is crucial for optimum gas sensitivity [7]. This highlights the importance of achieving well-controlled uniform single-layer graphene growth. To this end, we have shown that the graphene thickness uniformity can be significantly tuned by careful control of the EG/SiC morphology [8], in turn leading to high reproducibility of sensors [9] with outstanding performance [10]. However, graphene has limitations for certain gas sensor applications concerning operation temperature and fragility upon surface modification. Along this line, the technology of epitaxial growth of graphene on SiC offers a possibility to develop novel 2D systems beyond graphene. It has been found that specially reconstructed SiC surfaces offer a unique possibility to arrange metallic materials (e.g. Au, Pt, Pd) on the surface to form macroscopic, electrically-continuous 2D metals, which have potential benefits in terms of the ability to operate at higher temperature and to serve as a more robust template for functionalization compared to graphene, along with added catalytic properties, while maintaining the sensitivity inherent to 2D materials.

An area where high sensitivity is particularly needed is in air quality monitoring of toxic pollutants like nitrogen dioxide and hazardous volatile organic compounds (VOCs) in living environments due to the toxicity of some of these compounds upon long-term exposure even at trace concentrations like parts per billion (ppb). The World Health Organization (WHO) recently released a report stating that 570 000 children under the age of 5 die annually from respiratory infections attributable to air pollution, predominantly indoor [11]. As an example, benzene is a genotoxic aromatic compound that has been found to be carcinogenic at any concentration [12], and is especially associated with leukemia. There are no safe exposure limits for benzene in the last published WHO recommendations [12], however the European Air Quality Directive guidelines [13] recommend an exposure limit of 1.6 ppb. To mitigate their detrimental effects the concentration and distribution of these pollutants need to be monitored at trace concentrations.

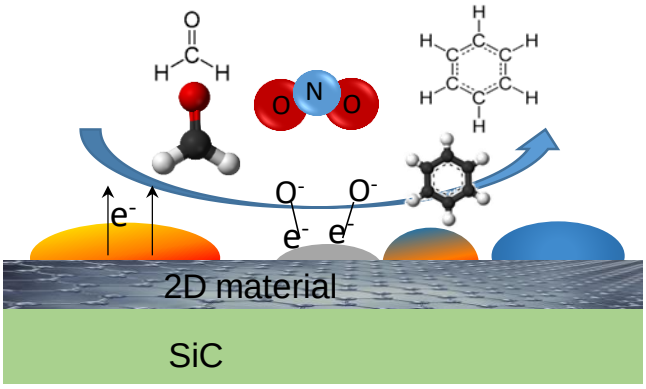

Figure 1: Schematic of sensitivity and selectivity tuning through 2D materials surface functionalization with nanoparticles.

In the future, air quality (AQ) assessment should ideally be based on real time monitoring of air pollutants with high spatial resolution, allowing pollution mapping and forecasting. This can only be achieved by utilizing low-cost monitoring devices of small size. Szulczynski et al. [14] and Spinelle et al. [15] recently studied currently commercially available low-cost sensors for VOC detection in outdoor and indoor air, with the latter focusing on benzene, and both concluded that current sensor technologies suffer from too high limit of detection and poor selectivity. Low cost sensors that can detect toxic VOCs at trace levels would thus constitute a breakthrough in the field of air quality monitoring (AQM).

In this study we propose a sensor platform (schematically illustrated in Fig. 1) based on 2D materials on SiC for detection of nitrogen dioxide (NO_2), formaldehyde (CH_2O), and benzene (C_6H_6) at concentrations of relevance to AQM. We explore functionalization with nanoparticles using a scalable 'soft' deposition approach that allows modifying the surface chemistry to generate sensitivity to specific target molecules without damaging the 2D sensor transducer. Additinally, we report on a smart sensor signal evaluation approach allowing fast response times, which could allow real-time monitoring of toxic pollutants in air.

2 METHODS

Epitaxial graphene was prepared by sublimation of SiC and subsequent graphene formation on semi-insulating, Si-terminated, 4H-SiC (0001) on-axis substrates at 2000 °C in argon and at a pressure of 1 bar [16]. Metal-oxide nanoparticles (NPs) were deposited onto EG/SiC using a hollow-cathode pulsed plasma sputtering technique where the particles grow in the gas phase [17].

A Dimension 3100 AFM with the Nanoscope IVa controller and Si tips (PPP-NCHR-50 from Nanosensors) was used in tapping mode to obtain topography images of the sensing layers. Raman spectroscopy and reflectance mapping were performed in a micro-Raman setup using an objective of 100X magnification, a CCD camera coupled to a monochromator (HR460), and solid-state laser excitation at 532 nm with a power of 17 mW focused to a spot with ~0.9 um diameter, and a spectral resolution of circa 5 cm^{-1}.

Chemiresistor sensor devices were fabricated by depositing electrodes on top of the 2D material surface through sequential DC magnetron sputtering of titanium (2 nm) and gold (200 nm). The electrodes are 1 mm wide with a 1 mm gap in between. The sensor chips were glued using Aremco Ceramabond 571 on top of ceramic heater substrates (Heraeus GmbH, Germany) with an additional Pt-100 temperature sensor (Heraeus GmbH, Germany). These structures were mounted on top of TO8-sockets and electrode-pin connections were realized using gold-wire bonding. The mounted sensors were inserted into a flow cell which is attached to a computer controlled gas mixing system. A dry background mixture of N_2 and O_2 with a ratio of 80:20 ml/min and a constant flow rate of 100 ml/min was used both as a carrier gas and purging gas. A UV LED (Sensor Electronic Technology Inc, S-T39B-F1-265-01-1-050) with a wavelength of 265 nm and an optical output power of 0.8 mW was integrated into the flow cell and used to irradiate the sensor surface during some measurements.

3 RESULTS AND DISCUSSION

3.1 Epitaxial Graphene on SiC

The response is defined as Response = $(R-R_0)/R_0$, where R is the saturated resistance signal and R_0 corresponds to the baseline resistance before the exposure. Fig. 2 shows the NO_2 response of three different sensors fabricated on as-

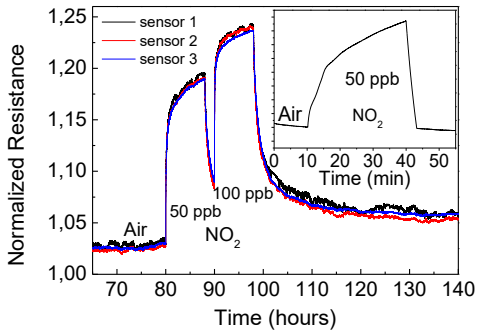

Figure 2: . Three different sensors processed on as-grown, uniform (99 %) monolayer graphene on SiC show device reproducibility in NO_2 detection at ppb level (reprinted with permission from [9]). The inset shows the response to 50 ppb NO_2 upon irradiation with a 265 nm UV LED.

grown, uniform ML (99 %, determined by reflectance mapping), demonstrating high device reproducibility with significant response to ppb concentrations. The response- and recovery times to NO_2 can be significantly improved by irradiating the sensor surface during gas exposure using an integrated UV LED (Fig. 2, inset).

3.2 Nanoparticle Functionalization

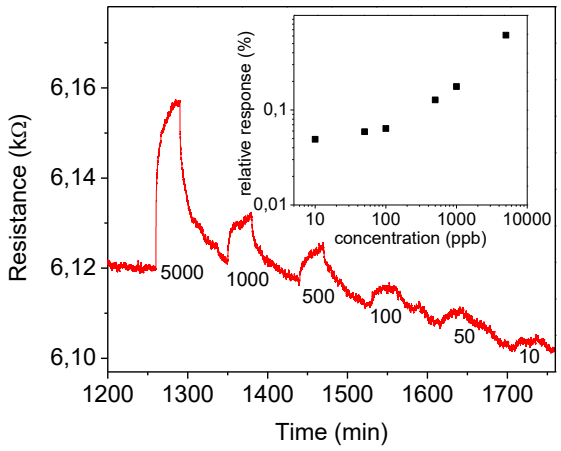

Figure 3: Sensor response of Fe_3O_4 decorated EG/SiC at 150 °C to benzene concentrations in the range 5000 ppb to 10 ppb.

A major challenge for AQ sensors is tailoring the materials to interact with a specific target analyte. This has been addressed, e.g., by combining graphene (for sensitivity) with metal/oxide nanoparticles (for selectivity). Concomitantly, functionalization or modification of the graphene often results in poor reproducibility. We have investigated the gas sensing performance of EG/SiC decorated with nanostructured metals and metal-oxide NPs (schematically shown in Fig. 1). Under the right deposition conditions the structure and electronic properties of the graphene remain intact, while the surface chemistry can be tuned to improve sensitivity, selectivity and speed of response to gases relevant for AQM, yielding detection at ppb concentrations of toxic gases such as nitrogen dioxide, benzene, and formaldehyde [9, 10]. Our optimal configuration for benzene detection (Fe_3O_4 NPs on graphene, Fig. 3) yields a concentration dependent response in the range 5000 ppb to 10 ppb.

However, precaution is needed when choosing the functionalization process in order not to modify the 2D transducer in such a way that its electronic properties are altered, thereby destroying the promise as an extremely sensitive sensing transducer. Fig. 4 shows Raman spectra (left) together with AFM morphology maps (right) of as-grown EG/SiC, as well as EG/SiC with TiO_2 NPs of low (monodispersed NPs) and high surface coverage. As can be seen, for graphene decorated with monodispersed TiO_2 NPs, the typical Raman peaks of graphene are intact. The features starting in the range of 1280 cm^{-1} and extending into the G-peak are all related to the interfacial buffer layer between the graphene and the SiC substrate [18], and while they overlap with the position of the D peak they are not related to defects. For TiO_2 of a high surface coverage, however, the D peak intensity is much more pronounced, and also the G and the 2D peaks are affected, suggesting deterioration of the graphene structure. The latter has a detrimental effect on the transducing properties of graphene and, thus, on the sensor performance.

3.3 2D Platinum on SiC

Despite its high sensitivity, graphene has limitations for certain gas sensor applications concerning operation temperature and fragility upon surface modification. Therefore, we are currently investigating atomically thin 2D platinum produced by templated growth on SiC. This transducer material has the advantage of being able to operate at higher temperature and to be more robust upon surface functionalization compared to graphene, while adding catalytic interaction with certain gas analytes. Fig. 5 shows the response of a 2D Pt on SiC sensor to CH_2O at 150 °C. The sensor was exposed for 30 minutes towards 50, 100, and 150 ppb, respectively, with 60 minutes of purging in background gas between the pulses. The response is significant in the tested range (i.e. the range relevant to AQ monitoring of CH_2O), with a concentration dependent response magnitude of 7 % to 50 ppb and 10.5 % to 150 ppb, and a signal to noise ratio (SNR) of 40.9 dB at 50 ppb, calculated based on a noise level of three times the standard deviation of the baseline signal (3σ). Such a high SNR suggests that the lower limit of detection is significantly better than the tested range.

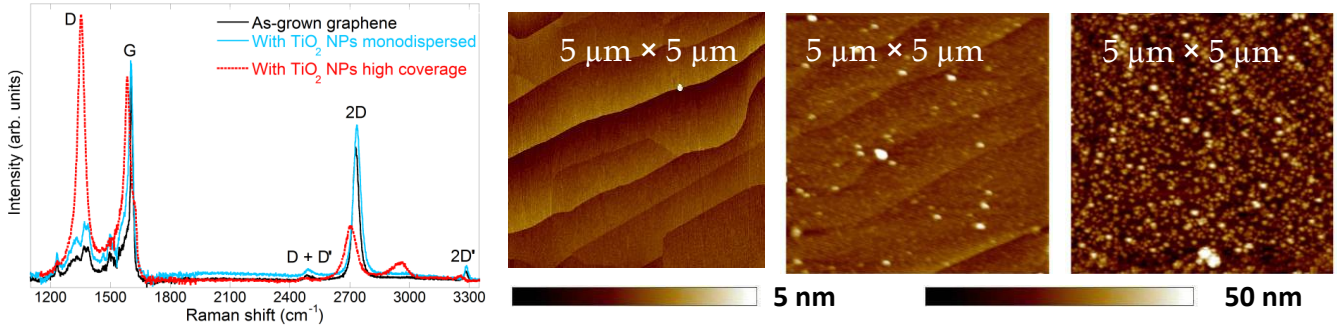

Figure 4: (left) Raman spectra and (right) surface morphology maps of as-grown epitaxial graphene on SiC, and EG/SiC decorated with TiO_2 NPs of differing surface coverage (from left to right in the morphology micrographs: as grown graphene, monodispersed NPs, high surface coverage of NPs).

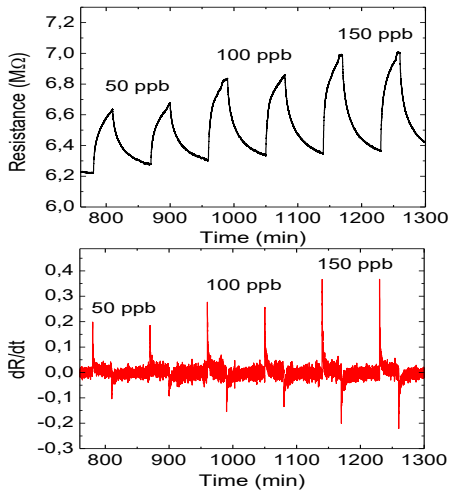

Figure 5: Response to CH_2O concentrations in the range 50 to 150 ppb at 150 °C; the lower panel shows the first order time derivative of the raw sensor signal.

3.4 Improving Speed of Response

For AQ monitoring it is desired to have a sampling rate and hence response time in the range of 30 seconds to a few minutes. The response time is normally defined as the time required to reach a certain percentage of the saturated response, e.g. the time it takes to change from 10 % to 90 % (τ90) of the saturated sensor response. However, gas concentration can also be evaluated based on the initial rate of change of resistance, dR/dt, during gas exposure [19]. Since adsorption sites can be occupied more quickly for larger gas concentrations, dR/dt is larger for higher concentrations, and at the same time independent on exposure time as long as the exposure exceeds the time needed to reach the maximum dR/dt. Therefore, rapid determination of gas concentration is possible by analyzing dR/dt. The lower panel in Fig. 5 shows the first order time derivate of the sensor signal after smoothening the data with a moving average filter. As can be seen, dR/dt exhibits distinct peaks in response to CH_2O and the peak values are concentration dependent. The response time, defined here as the time it takes to reach the maximum dR/dt value during exposure, is in the range 10-30 seconds, compared to tens of minutes for the τ90 response of the raw sensor signal. Furthermore, the magnitude of the negative peaks corresponding to desorption are also proportional to the concentration, whereby dR/dt can be used for both increasing and decreasing concentrations. Consequently, dR/dt could be used to generate a significantly faster response, enabling the desired sampling rate for AQ monitoring, while maintaining ppb level sensitivity.

4 SUMMARY

We studied a sensor platform based on 2D materials on SiC and have demonstrated detection of nitrogen dioxide, formaldehyde, and benzene in the parts per billion regime. The sensitivity to specific target molecules is strongly influenced by the surface functionalization and the type of 2D material transducer. This, combined with a smart sensor signal evaluation approach allowing fast response times, could allow real-time monitoring of toxic pollutants at concentrations of relevance to air quality monitoring.

5 ACKNOWLEDGEMENTS

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