

# Metal Oxide Nanolayer Decorated Epitaxial Graphene Gas Sensors for Air Quality Monitoring

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## Summary:

Metal or metal oxide decorated two-dimensional material hybrids have been shown to exhibit excellent sensitivity performances if used as chemical gas sensors. We investigated the influence of operating temperature, relative humidity and UV irradiation of various metal oxide nanolayer decorated epitaxial graphene hybrid sensors during exposure to several gases of interest for air quality monitoring. Furthermore, a data treatment method is introduced to further enhance sensor properties.

**Keywords:** metal oxide, nanolayer, epitaxial graphene, chemical gas sensor, air quality monitoring

## Background

Two-dimensional materials like graphene exhibit several excellent properties, which allow the fabrication of gas sensors that can be used for detection of very small gas concentrations. Epitaxially grown graphene on SiC was found to be more sensitive when used as a transducer in a gas sensor than commercially available graphene produced through chemical vapor deposition (CVD) [1]. One method to increase the sensitivity and/or selectivity to specific gases, is the combination of various sensing materials or the decoration of a transducer with a metal oxide nanostructure on top [1,2]. Here, we show that combining epitaxial graphene on SiC with nanolayers (NLs) of well-studied sensing materials leads to enhanced sensitivity towards several gases of interest for air quality monitoring.

## Method and materials

Metal oxide decorated epitaxial graphene hybrids have been produced. Nanolayers (few atoms thick) of copper oxide (CuO), iron oxide (Fe<sub>3</sub>O<sub>4</sub>), vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) and zirconium dioxide (ZrO<sub>2</sub>) have been used as decoration materials, deposited with pulsed laser deposition [1]. The sensor resistance is measured over time and the response is defined as the difference in % between the saturated/last resistance signal compared to the baseline resistance before gas exposure. The response of the different hybrid sensors towards gases of interest for air quality monitoring with changing operating temperature, relative humidity and irradiation with UV light during the gas measurements was studied. To speed up the sensor response,

the first-order time-derivative of the sensor signal is used as an additional response signal.

## Results

Normally, chemical gas sensors need a certain operating temperature before they react with the target gas and an increase in temperature (up to a limit) means an increase in response. An exposure at 50, 100, and 150 °C at zero relative humidity (RH) towards 200 ppb benzene (C<sub>6</sub>H<sub>6</sub>) and formaldehyde (CH<sub>2</sub>O) shows that only at 150 °C, all four sensors were able to sense both gases. While CuO was able to detect gas pulses even down to 50 °C, Fe<sub>3</sub>O<sub>4</sub> and V<sub>2</sub>O<sub>5</sub> needed at least 100 °C. In contrast, for an exposure towards 25 ppm ammonia (NH<sub>3</sub>) at 50 %RH, at 50, 75, 100 and 125 °C, only ZrO<sub>2</sub> has its highest response at 125 °C, while all other sensors exhibit the highest response as 50 °C. While a higher sensor response is normally desired, this can be offset by disadvantages like slower time constants or increased signal noise. For example, only exposures at 125 °C lead to a steady-state response during the 30 min gas exposure.  $\tau_{63}$ , extrapolated using an exponential fit, gradually increases from approximately 150 s at 125 °C up to 550 s at 50 °C on average.

Besides the operating temperature, relative humidity in the ambient can be another critical parameter for the sensor response of some material/gas combinations. It is known that many metal oxides exhibit a cross-sensitivity towards RH and a higher level of RH in the ambient usually results in a lower gas sensitivity, as the target gas molecules compete with water molecules for available adsorption sites. An exposure towards 200 ppb of C<sub>6</sub>H<sub>6</sub> and CH<sub>2</sub>O with

50 %RH leads to a decrease in response of on average about one order of magnitude compared to dry conditions.  $V_2O_5$  does not react at all when humidity is introduced. For the case of  $NH_3$ , all sensors except the one functionalized with  $V_2O_5$  exhibit a decrease in sensitivity when changing from a dry to a humid environment, e.g. 20 %RH. A further increase in humidity increases the response again for some samples, even exceeding the response at 0 %RH ( $ZrO_2$ ). This increase in response with increasing RH and the increase with lower temperatures could be due to a reaction with OH groups or of products of reactions from OH groups and  $NH_3$ , leading to a higher overall response, which is not necessarily only related to the  $NH_3$  exposure itself. This phenomenon was shown to occur for metal oxide gas sensors when operating them at relatively low temperatures in a humid environment [3,4].

The sensitivity and speed of response of a chemical gas sensor was shown to be enhanced through UV irradiation for many different material/gas combinations [5]. Moreover, it was shown that UV irradiation can be used to clean graphene surfaces, thus freeing active sites for target gas interaction [6]. Figure 1 summarizes the responses towards a 30 min exposure of 25 ppm  $NH_3$  at 50 %RH without and with the influence of 355 nm UV irradiation. A clear trend can be observed as the relative sensor response is highest with UV irradiation and decreases with no irradiation for all sensors except  $ZrO_2$  for which the response stays approximately constant. Changing the UV irradiation wavelength from 355 to 265 nm has no significant effect on the sensor response magnitude for the tested materials. However, the shorter wavelength, with its higher energy level, has a stronger impact on the speed of response.

A method to additionally achieve faster time constants is the use of the sensor signal's first-order time-derivative [7]. This is exemplarily shown as the red (lower) curve in Fig. 2, where a  $Fe_3O_4$  NL decorated epitaxial graphene sensor was exposed to 25 and 100 ppm of  $NH_3$  at 75 °C at 50 %RH. The peaks arrive much faster and are also concentration dependent, making it useful as a feature in multivariate analysis [7,8]. Moreover, this signal is more robust against varying exposure and relaxation times with a very stable baseline.

Chemical gas sensors are highly tailorable systems. Exploiting the excellent sensitivity of epitaxial graphene, combining it with a nanostructured metal oxide and adjusting the measurement conditions accordingly to the desired application can lead to high performance gas sensor devices.

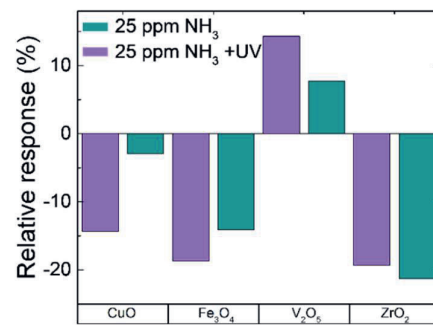


Fig. 1. Relative response towards 25 ppm  $NH_3$  with and without 355 nm UV irradiation.

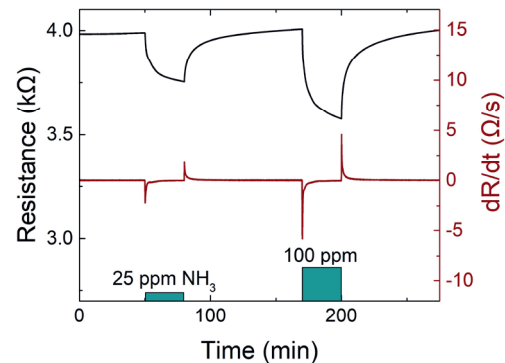


Fig. 2. Resistance over time (upper black) of  $Fe_3O_4$  NL decorated epitaxial graphene sensor with corresponding first-order time-derivative signal (lower red) towards 25 and 100 ppm  $NH_3$  at 75 °C and 50 %RH.

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