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Abstract

Selective Detection of Toxic Gases by Arrays of Single-Layer Graphene Sensors Functionalized with Nanolayers of Different Oxides †

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Abstract: Graphene provides an ideal platform for chemiresistive gas sensors as the material is fully exposed to the surrounding environment. For practical use in an ambient atmosphere, its sensitivity and selectivity should be evoked by functionalization by defects and dopants or by decoration with nanophases of metals or metal oxides. Here, we demonstrate a few successful cases of selectivity enhancement by functionalizing the graphene with different oxide layers and applying machine learning to the resulting sensor array.

Keywords: graphene; gas sensor; laser deposition; functionalization; sensor array; electronic nose

1. Introduction

Chemiresistive graphene gas sensors are appealing for e-nose applications where their easy production and miniaturization potential can be exploited. Relevant use cases include monitoring indoor and outdoor air quality, performing medical self-diagnosis by breath analysis, and controlling industrial processes. However, for effective use in practical sensors, the sensing properties of graphene have to be improved and controllably modified. We have shown nearly a 100 times enhancement of graphene's gas sensitivity as well as improved selectivity through functionalization by pulsed laser deposition [1,2]. In this work, we demonstrate the modification of graphene with different metal oxides to controllably induce partial selectivity toward the harmful gases NH3, H2S, NO2, and O3. Selected combinations of these sensors were integrated into arrays, whereby machine learning applied to the output signal pattern of each array allowed the successful differentiation of various gases and their mixtures.

2. Materials and Methods

Chemically vapor-deposited single-layer graphene was transferred onto Si/SiO2 electrode substrates (inset in Figure 1) or special CMOS sensor substrates with built-in microheaters. A KrF excimer laser was used to deposit thin oxide layers on top of the graphene from respective ceramic targets [1]. The substrate temperature, background gas type and pressure, and the thickness of the functionalizing layer were optimized for the best performance of the sensors.

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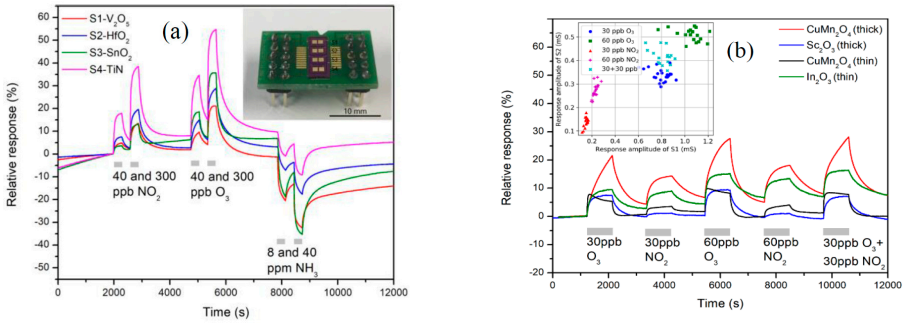

Figure 1. (**a**) Responses of an array (inset) of graphene sensors functionalized with different PLD films for differentiating NH3 and NO2 gases. Measured at RT under UV light excitation. (**b**) Responses of an array of graphene sensors functionalized with different PLD films for differentiating O3 and NO2 gases. The inset shows clustering of the data points in the 2D feature space of the response amplitudes.

3. Discussion

Figure 1a shows the responses of the individual sensors in an array for the simultaneous detection of NO_2 and NH_3 gases. The functionalizing materials were chosen to achieve partial selectivity of the individual sensor, either toward NO_2 (TiN, HfO_2) or NH_3 (V_2O_5, SnO_2). For machine learning studies, an extended (>50 h) gas sensing experiment was carried out, where NO2 and NH3 were simultaneously present and their concentrations in synthetic air were randomly (but gradually) changing within 25–390 ppb and 4.5–80 ppm, respectively. Simple artificial neural networks (containing a few neurons in a single hidden layer) applied to the sensor array containing three of the most stable sensors could reliably distinguish and quantify NO2 and NH3 in a mixture over a period of tens of hours, maintaining the mean relative error $\leq$14%.

Figure 1b shows the responses of the individual sensors in another array tailored for differentiation between O_3 and NO_2 gases. Although all the tested materials showed selectivity toward O_3, functionalizing materials were selected to exhibit different response ratios to O_3 and NO_2 gases. During 72 h, the sensors were exposed to randomly generated concentration cycles of 30 ppb NO_2, 30 ppb O_3, 60 ppb NO_2, 60 ppb O_3, and 30 ppb NO_2 + 30 ppb O_3 in synthetic air. Various properties of the dynamic responses (amplitude, response rate, and recovery rate) were considered features for machine learning, enabling clearly distinguishing these five gas compositions with an accuracy of ~94%.

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

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