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Adjusting the electronic properties and gas reactivity of epitaxial graphene by thin surface metallization



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ABSTRACT

Graphene-based chemical gas sensors normally show ultra-high sensitivity to certain gas molecules but at the same time suffer from poor selectivity and slow response and recovery times. Several approaches based on functionalization or modification of the graphene surface have been demonstrated as means to improve these issues, but most such measures result in poor reproducibility. In this study we investigate reproducible graphene surface modifications by sputter deposition of thin nanostructured Au or Pt layers. It is demonstrated that under the right metallization conditions the electronic properties of the surface remain those of graphene, while the surface chemistry is modified to improve sensitivity, selectivity and speed of response to nitrogen dioxide.

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1. Introduction

Graphene attracts huge interest due to its unique and rich electronic and optical properties [1], such as enormous carrier mobility and optical transparency, as well as flexibility, robustness, environmental stability, and tunable wettability [2]. Graphene research has been predominantly focused on fundamental physics and electronic devices. The potential applications of graphene span a much broader field that includes also sensors, photonics and optoelectronics, where the combination of the optical and electronic properties can be fully exploited.

Graphene gas sensors have been explored since 2007 [3] and impressive sensitivities to various molecules have been achieved in graphene produced by mechanical exfoliation [3], chemical vapor deposition [4], reduced graphene oxide [5], and we have previously demonstrated NO₂ detection limits in the low parts per billion (ppb) range for epitaxial graphene on silicon carbide (SiC) [6]. Concomitantly graphene has low selectivity due to high sensitivity to a range of gas molecules, like NO, NO₂, CO, CO₂, NH₃, and H₂O, which are all of interest for industrial, environmental and medical applications. It also suffers from slow adsorption/desorption, leading to slow response/recovery times.

For graphene-based sensors to become useful it is important to improve selectivity, response/recovery times, and to a certain extent also reproducibility. To that end, several approaches based on surface modifications of the graphene have been investigated. Very impressive detection limits for NO and NO₂ in the range of parts per trillion and

even parts per quadrillion have been demonstrated by the use of constant ultraviolet irradiation [4]. However such treatment causes a semi-reversible oxygen functionalization that breaks the sp² hybridization of the graphene [7]. A study by Mao et al. found that the sensitivity to NO₂ can be enhanced while suppressing response to other gases like NH₃ by decoration with tin oxide nanocrystals [8], though this technique leads to poor time constants and poor reproducibility. A density functional theory (DFT) investigation [9] concluded that impurity doping of graphene by nitrogen or boron can be used to improve sensitivity and selectivity towards CO, NO, NO₂ and NH₃, due to increasing the adsorption energy of specific molecules. On the other hand, this approach may not be practical since increasing the adsorption energy increases the recovery time in an exponential manner.

In this study we investigate a reproducible means of functionalizing graphene with nanostructured metals by sputter deposition. Graphene grown by sublimation of SiC [10] was decorated with thin (nominally 2–5 nm) layers of Au and Pt and the effect of these metallizations on the electronic properties of the graphene as well as their potential use in controlling gas adsorption and chemical reactions occurring at the graphene surface were investigated. The gas response was tested towards common pollutants from combustion engines and in power plant flue gases, specifically NO₂, CO, H₂, and NH₃.

2. Material and methods

Large area epitaxial graphene (EG) 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 [10]. Thin layers (2–5 nm) of

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nanostructured Au or Pt were deposited onto the graphene by direct current magnetron sputtering at room temperature at an elevated pressure of ≈ 50 mTorr and a power of ≈ 100 W.

The effect of the metallization on the electronic properties of the graphene surface were studied by atomic force microscopy coupled with surface potential mapping by scanning Kelvin probe microscopy (SKPM), which can be used to study nanoscale variations in the graphene thickness [11] due to the difference in work function (ϕ) depending on the graphene layer thickness. The stability of SKPM measurements relies on the stability of the work function of the probe tips, and is sensitive to the measurement environment, such as humidity. For comparison of relative work function shifts between samples before and after metallization, average ϕ values were instead determined by measurements in an ambient Kelvin probe, which determines ϕ over a much larger area (determined by the tip radius of 0.5 mm). The work function of the tip is calibrated against a gold standard with a known work function and the values calculated are more stable as the tip never comes in contact with the sample, thereby avoiding contamination and tip deformation. Variations in ambient humidity influence the graphene work function more than that of the gold reference electrode. Therefore only the relative shifts between different samples determined during the same measurement run (i.e. in the same environmental conditions) are compared.

Chemiresistor sensor devices were manufactured on the graphene on SiC (EG/SiC) structures by deposition of Pt contact pads and mounting onto a 16 pin sensor header with integrated heater and temperature sensor (see inset in Fig. 2a). Experimental details of the sensor preparation are reported elsewhere [6]. Gas sensing measurements were conducted under laboratory conditions, using an in-house gas mixing system that comprised mass flow controllers (Bronkhorst High-tech B.V. Netherlands, model F-201C-RA-11-V 100 ml/min). Sensing characteristics in terms of sensor signal, response and sensitivity [12] were studied through the detection of NO₂ concentrations ranging from 10 ppb to 500 ppb, and CO, H₂, and NH₃ concentrations ranging from 40 parts per million (ppm) to 500 ppm.

The carrier gas (the background gas during test pulses and the gas present at the sensor surface in between test pulses) for all of the gas exposure tests was simulated air (20% oxygen and 80% nitrogen). The total flow was maintained constant at 100 ml/min. The temperature of the sensors during gas testing was varied from room temperature (RT) to 100 °C. The resistance was measured using a Keithley 2000 multimeter configured in the two-wire mode.

3. Results and discussion

Fig. 1 presents SKPM maps showing surface morphology and surface potential for as-grown graphene (a), after sputter deposition of nanostructured Au of ≈ 5 nm (b), ≈ 2 nm (c), and Pt of ≈ 5 nm

(d). The graphene morphology is characterized by wide terraces due to the SiC step-bunching during the growth, whereas the differing contrasts in the surface potential map correspond to areas of single- or bilayer graphene (1LG, 2LG), due to their differing work functions [13].

After Au deposition the morphology is rougher due to the formation of Au grains (see inset in Fig. 1b). However, the surface potential still shows sharp contrast between 1LG and 2LG, meaning that the electronic properties of the surface remain those of graphene as opposed to those of a metal, which would have a uniform surface potential. While the contrast between 1LG and 2LG is still visible after metallization, the value of the surface potential difference has dropped from about 35 meV, which is typically measured for as-grown EG [13], to about 15–20 meV for 2 nm of Au and to 5–10 meV for 5 nm of Au. This difference in surface potential likely arises from different carrier concentrations in the graphene before and after metallization, altering the work functions of 1LG and 2LG differently. For the sample decorated with Pt the situation is different; the morphology indicates that Pt wets the graphene surface and forms a continuous porous film, and the surface potential shows an almost uniform distribution, indicating that the Pt screens the graphene surface.

Decoration with thin layers of Au and Pt was also found to alter the carrier concentration of the graphene. Work function measurements indicate that both Au and Pt n-dope the graphene (lower the work function and thus increase the Fermi level, E_F). The as-grown EG/SiC is n-type doped due to electronic coupling with the SiC substrate [14]. The carrier concentration in EG/SiC varies depending on the growth conditions [15], but in our material it is normally in the range of 10^{12} cm⁻² [13,16]. This doping can become an issue for chemiresistor sensors if gas interactions withdraw enough electrons for the Fermi level to crossover the Dirac point where the conduction band and valence band meet, bringing about a transition from n-type to p-type conduction and as a consequence a change in the sensor response direction [6]. The relative shifts (compared to an as-grown sample) in E_F due to the metallization, determined from the measured work function differences, along with corresponding carrier concentrations (calculated from ΔE_F) are summarized in Table 1. As can be seen, ΔE_F is larger for decoration with Au compared to Pt. Intuitively one would assume that the crossover point from n- to p-type doping would be when the metal work function (ϕ_M) is equal to that of graphene (4.5 eV). However, it was found that both Pt ($\phi_M \approx 6.1$ eV [17]) and Au ($\phi_M \approx 5.5$ eV [17]) n-dope the graphene. This result is in disagreement with a study of Giovannetti et al., in which theoretical calculations based on DFT predicted n-type doping for Au and p-type doping for Pt [17]. However, it should be pointed out that the study of Giovannetti et al. investigated dense metal films and not thin, porous layers of a few nanometers.

From Table 1 it can be inferred that the shift in E_F due to charge transfer from the deposited metal depends on the metal thickness and the difference between ϕ_M and ϕ , where a larger difference

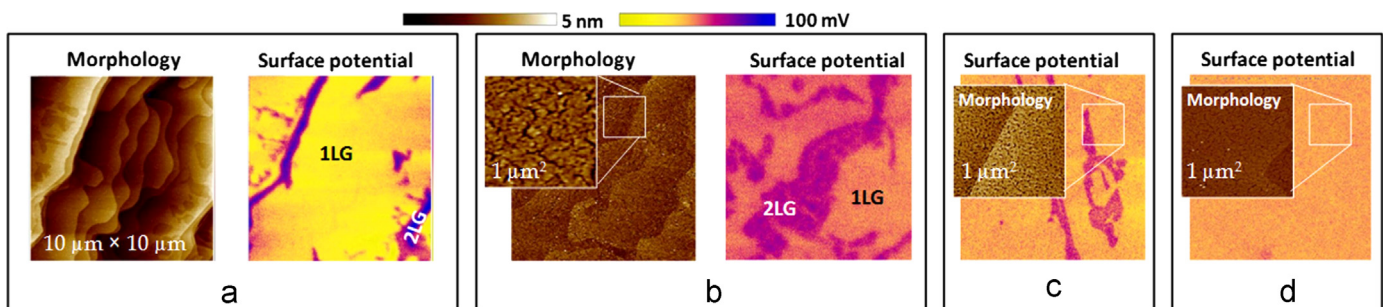


Fig. 1. Effects of metallization on morphology and surface potential. Graphene surface morphology and surface potential for the as-grown sample (a), after deposition of ≈ 5 nm (b), ≈ 2 nm (c), and of nanostructured Au and ≈ 5 nm of Pt (d). The scan size is $10 \mu\text{m} \times 10 \mu\text{m}$ (insets are $1 \mu\text{m} \times 1 \mu\text{m}$).

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