



Effects of humidity on the electronic properties of graphene prepared by chemical vapour deposition



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ABSTRACT

The effects of humidity on the electronic properties of mono- and bi-layer graphene prepared by chemical vapour deposition and transferred on SiO₂ are investigated via simultaneous global transport and local work function measurements using the van der Pauw method and Kelvin probe force microscopy, respectively. It is found that mono-layer graphene on SiO₂ is extremely sensitive to water vapour, with water molecules acting as physisorbed loosely bound p-dopants. In the case of a bi-layer stack, produced by double transfer of two graphene layers, the layers are randomly oriented and decoupled with respect to each other. As a consequence, the bottom layer of the bi-layer stack is mostly affected by substrate charges, while the top graphene layer behaves as a decoupled layer, which is externally doped by the water vapour. Moreover, we provide evidence that ambient humidity is only partly responsible for the p-doping of graphene. These findings will assist in the development of reliable graphene-based electronics such as sensors working in ambient air.

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1. Introduction

The two-dimensional nature of graphene and exceptional electronic and mechanical properties as well as the unique high surface-to-volume ratio of graphene have been proven to be the deciding factors for the implementation in electronic applications such as transistors, touch screens and sensors [1]. With water vapour being a substantial component of the ambient air, graphene-based devices designed to operate in ambient air (e.g. sensors) will be significantly affected, as their electronic properties, such as carrier concentration, resistance and mobility, will change with humidity. For successful commercialisation of graphene-based devices, the complete understanding of the water-graphene interactions is necessary, in an attempt to appropriately calibrate or encapsulate them in order to minimize the effect of ambient humidity.

Furthermore, it has been shown that AB stacked bi-layer epitaxial graphene on SiC has a different response to water,

compared to mono-layer graphene [2–4]. Likewise, previous theoretical and experimental works have proven that both substrate and environmental exposure are responsible for the doping in graphene [5–7], while free-standing graphene is charge neutral [7]. In the case where graphene is prepared by chemical vapour deposition (CVD) and transferred on SiO₂, the underlying substrate, polymer residues and environmental doping result in the high hole concentration often observed in this type of graphene [6–8]. Moreover, water trapped between the substrate and graphene [9–11] as well as substrate charge inhomogeneities [12] act as scattering centres. These degrade the carrier mobility of the transferred graphene. Most importantly, the well-known hysteresis effect observed in graphene field effect transistors on SiO₂ has been attributed to doping species such as H₂O and O₂ inevitably trapped both at the graphene/substrate interface and on graphene surface [9]. These trapped impurities, caused by the transfer procedure in ambient conditions, are responsible for inconsistency in the performance of graphene transistors. To overcome these unwanted effects, several post-growth procedures have been developed. Here, we use thermal annealing of the transferred graphene in vacuum or inert atmosphere [13]. This has the two-fold advantage of minimizing poly methyl-methacrylate (PMMA) residues, induced by the

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transfer process and any trapped water between the graphene and substrate interface. However, to completely avoid exposure of the graphene surface to doping species, encapsulation with other 2D materials such as hexagonal boron nitride (h-BN) would be required [14,15] (this topic is outside of the scope of this study).

Despite the great efforts to study the combined effects of substrate and environment on the electronic properties of graphene using bulk electronic measurements [16], Raman [9] and density functional theory (DFT) calculations [17], there is still a lack of understanding of the environment and substrate-induced effects. In an attempt to gain such understanding for a more technologically-oriented type of graphene, we employ simultaneous Kelvin probe force microscopy (KPFM) and transport measurements in the van der Pauw geometry, to investigate the effects of controlled variable humidity (R.H. = 0–60%) on the local and global electronic properties of CVD graphene samples. KPFM is capable of measurements of the surface potential of the sample that provides essential information about charge variation, work function and therefore layer distribution in graphene with nanometre resolution. On the other hand, the bulk transport measurements provide a global carrier concentration value throughout the 10×10 mm graphene sample, which is an ideal and rapid characterisation technique for large samples. Both types of measurements are performed simultaneously in a well-controlled environment of the scanning probe microscope (SPM) enclosure by varying the environmental conditions from ambient (~ 23 °C, R.H. $\sim 35\%$), vacuum ($\sim 1 \times 10^{-5}$ mbar), dry nitrogen (of 99.9995% purity) and gradually increased humidity (0–60%). Complementary Raman characterisation has also been employed to evaluate the graphene layer structure of the mono- and bi-layer graphene on SiO₂.

2. Methods

2.1. Sample preparation

The mono-layer graphene synthesis was carried out using copper (Cu) foil as the catalyst in a cold walled Chemical Vapour Deposition (CVD) reactor (Aixtron BM). After the synthesis, a PMMA sacrificial support layer was spin coated onto the graphene covered Cu foil. The Cu was etched using a ferric chloride containing solution. The film was cleaned with distilled water several times and transferred onto 300 nm SiO₂/Si substrate. In general, the PMMA can be removed either by using solvents or by annealing at 450 °C. It is well-known that after the use of chemical solvents some polymer residue is still present on graphene films. Thus, in order to have cleaner films, it was decided to remove the PMMA by thermal annealing at 450 °C for 2 h in N₂. A description of the graphene samples is presented in Table 1.

Bi-layer graphene samples were produced by individual stacking of 2 mono-layer graphene films. The second mono-layer graphene was transferred on top of the first one onto 300 nm SiO₂/Si substrate and the PMMA was again removed by thermal annealing. It is noteworthy to mention that the 2nd layer is placed in a random orientation in relation to the 1st layer, which

results in the non-AB stacking of the layers. The structural quality and morphology of all the graphene samples will be discussed below. Results of Raman characterisation are presented in Fig. 1 and a large-scale morphological characterisation of the transferred graphene is presented in Supplementary information (Fig. S1).

2.2. Raman spectroscopy

The Raman maps were obtained using a Horiba Jobin-Yvon HR800 system in order to investigate the structure of graphene samples. The 532 nm wavelength laser was focused through a 100× objective lens onto the graphene sample. For the mono-layer graphene, Raman spectra were obtained using a 600 gr/mm grating and normalized to the Si peak (~ 520 cm⁻¹). The Raman maps were obtained by collecting 10,201 individual spectra of ~ 300 nm lateral resolution. For the bi-layer the same grating was used, but the spectra were not normalized.

2.3. Transport measurements in van der Pauw geometry

A transport measurement system in the van der Pauw geometry compatible with SPM setup and environmental chamber was developed and allowed for carrier concentration measurements on the entire 10×10 mm² graphene sample. This allows to avoid patterning of devices and associated microfabrication steps, which are responsible for introducing further polymer residues, contamination and doping of the graphene. The sample was placed on the van der Pauw stage over a permanent NdFeB magnet creating a magnetic field of 370 mT. The resistivity (ρ) was calculated using:

$$e^{-\frac{\pi R_A}{\rho}} + e^{\frac{\pi R_B}{\rho}} = 1$$
, where R_A and R_B are the resistances obtained by applying a bias current $I_B = 120$ μ A and measuring the voltage drop across the opposite sides of the sample. To obtain the carrier concentration ($n = 1/eR_H$), the Hall coefficient (R_H) was measured using $R_H = V_H/B_I$ by applying current and measuring the diagonal Hall voltage (V_H) of the sample [18,19].

2.4. Frequency modulated Kelvin probe force microscopy

A NT-MDT Ntegra Aura SPM system equipped with an environmental chamber was employed in single pass frequency modulated Kelvin probe force microscopy (FM-KPFM) mode. In this tapping mode, a doped silicon probe (PFQNE-AL) with spring constant $k \approx 0.4$ – 1.2 N m⁻¹ is oscillating at its mechanical resonant frequency $f_0 \approx 300$ kHz, while a much lower frequency ($f_{mod} \approx 3$ kHz) modulating AC voltage is applied to induce a frequency shift of $f_0 \pm f_{mod}$ [20–23]. The side lobes (monitored by a PID feedback loop) generated by this shift are minimized by applying a DC compensation voltage. By measuring this DC voltage at each pixel, a surface potential map [contact potential difference (U_{CPD})] is constructed. As FM-KPFM is a force gradient technique, a high spatial resolution of <20 nm can be achieved, which is limited only by the tip apex diameter [24]. This allows nanometre resolution imaging of the surface potential of graphene and provides direct

Table 1
Graphene sample description.

Sample	Number of graphene layers	Post-growth transfer	Post-growth treatment
Mono-layer	Predominantly mono-layer graphene with 2LG islands	Transferred on 300 nm SiO ₂ /Si	Thermal annealing at 450 °C in N ₂
Bi-layer	Predominantly bi-layer graphene	Double transfer of two mono-layers on 300 nm SiO ₂ /Si	Thermal annealing at 450 °C in N ₂ , following each successive transfer

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