Toward Tunable Doping in Graphene FETs by Molecular Self-Assembled Monolayer

Bing Li,[a] Klekachev Alexander,[b,d] Mirco Cantoro,[b] Cedric Huyghebaert,[b] Andre Stesmans,[d] Inge Asselberghs,[a,b] Stefan De Gendt*[b,c] and Steven De Feyter*[a]

[a] Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium. Fax: +3216327990; Tel: +3216327921; E-mail: steven.defeyter@chem.kuleuven.be
[b] IMEC, Kapeldreef 75, B-3001 Leuven, Belgium. Tel: +3216281386; E-mail: Stefan.DeGendt@chem.kuleuven.be
[c]Division of Molecular Design and Synthesis, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.
[d]Department of Physics, KU Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium.

Supporting Information:

Various concentrations of OA solution were applied on HOPG by spin coating at the same spin speed of 2k rpm. As the AFM images in Figure S1 demonstrate, with increasing the OA concentration, the OA SAM coverage gradually increases from a partial coverage (Figure S1A and S1B) towards full coverage (Figure S1C) on HOPG. Further increase of the concentration results in multilayer formation (Figure S1D) or even thicker films (Figure S1E). Figure S1E shows some lower lying domains or islands embedded in a thicker film. The corresponding enlarged AFM image in Figure S1F reveals that these "islands" are actually monolayer or few-layer patches containing regular nanostripes of OA.

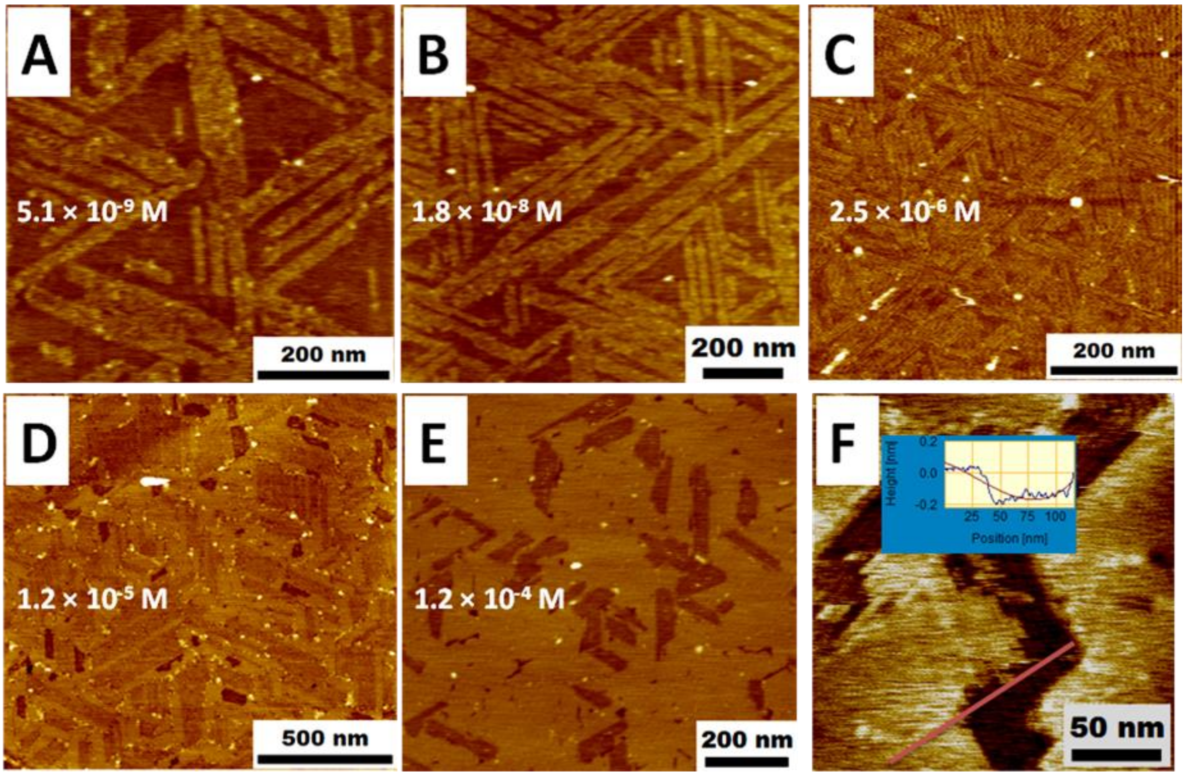

Figure S1. AFM height images of self-assembled monolayers of OA on HOPG prepared with OA concentration of 5.1×10^{-9} M, 1.8×10^{-8} M, 2.5×10^{-6} M, 1.2×10^{-5} M and 1.2×10^{-4} M for A, B, C, D and E respectively. (A and B) OA SAM partially covering HOPG. (C) OA SAM covering entire surface of HOPG. (D and E) OA multilayer on HOPG. (F) Enlarged image corresponding to (E) shows nanostripes in the few-layer islands and a height profile along the red line.

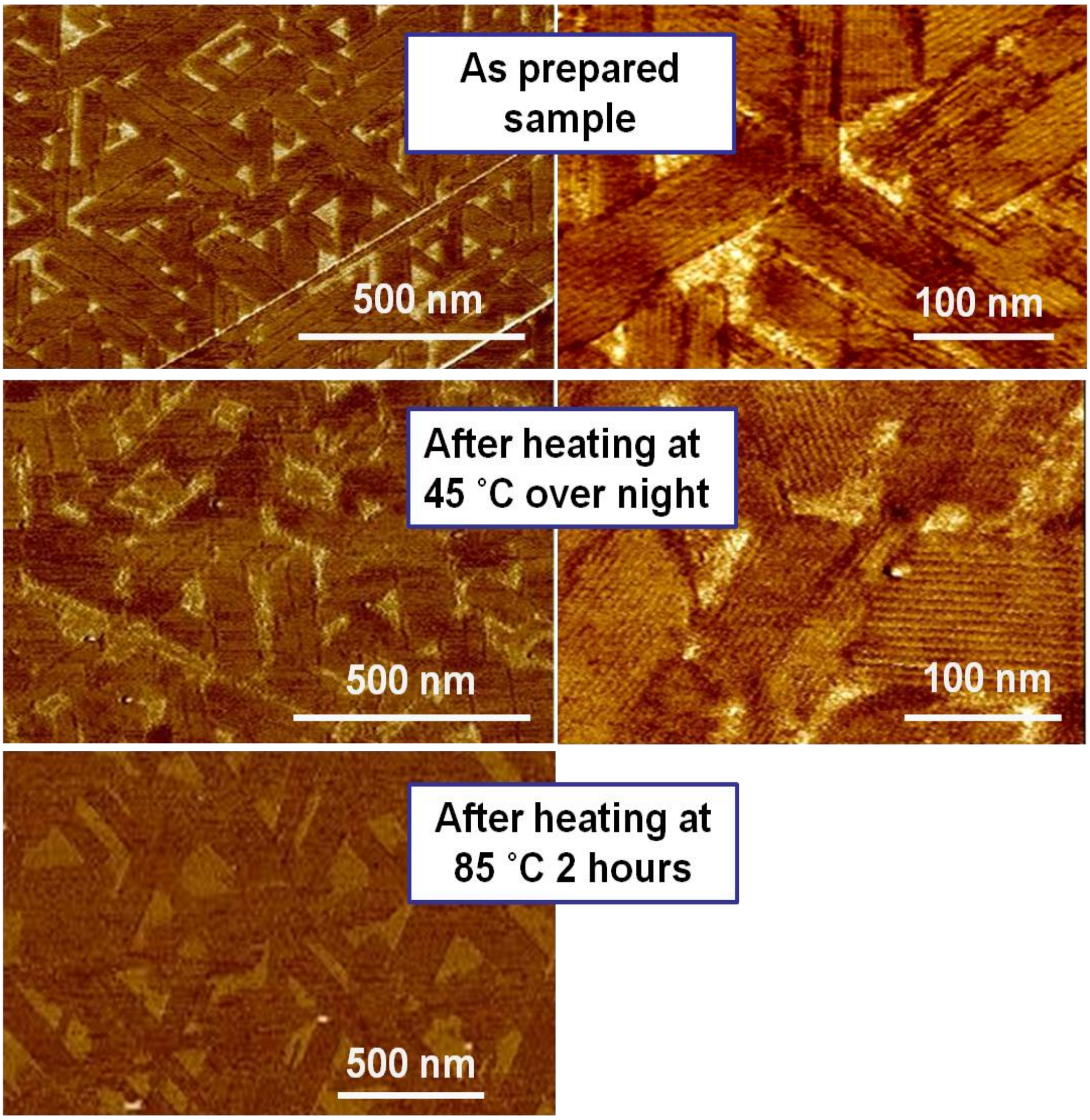

Figure S2. AFM phase images of self-assembled monolayers of OA on HOPG before and after different heat treatment conditions.

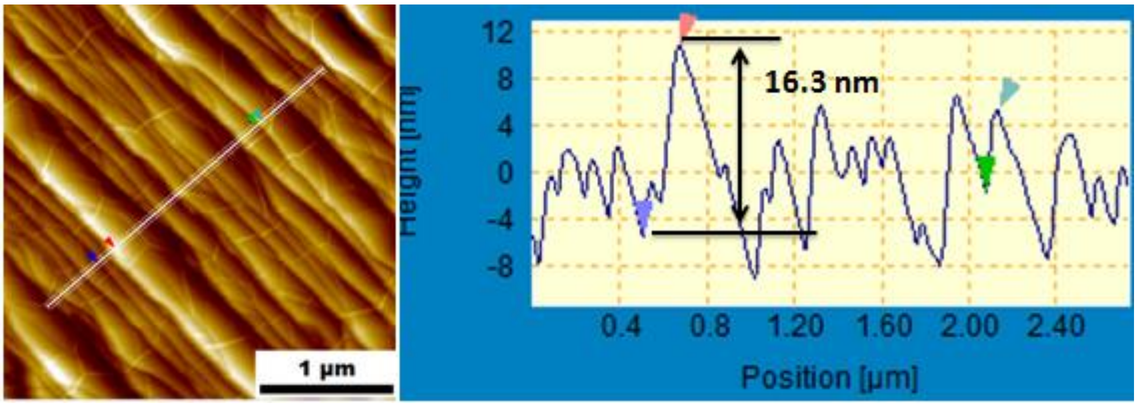

Figure S3. AFM height image of graphene surface on SiC substrate (left) and corresponding height profile (right) along the white line indicated in the AFM image.

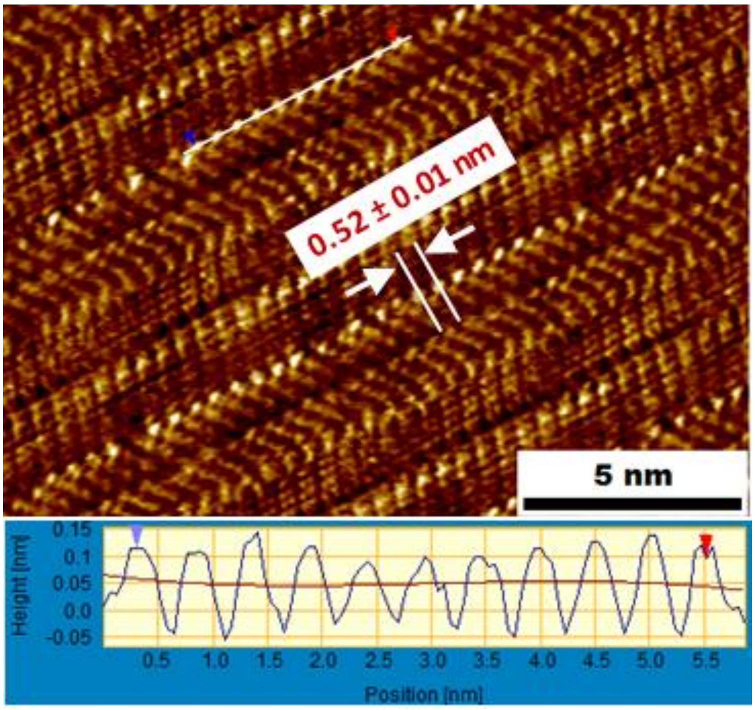

Figure S4. A high resolution STM image of self-assembled monolayer of OA on HOPG and corresponding line profile along the white line indicated in the image. The distance between two neighboring molecules is indicated in the image. The measurement conditions, I_{set} = 80 pA, $V_{set} = -650$ mV.

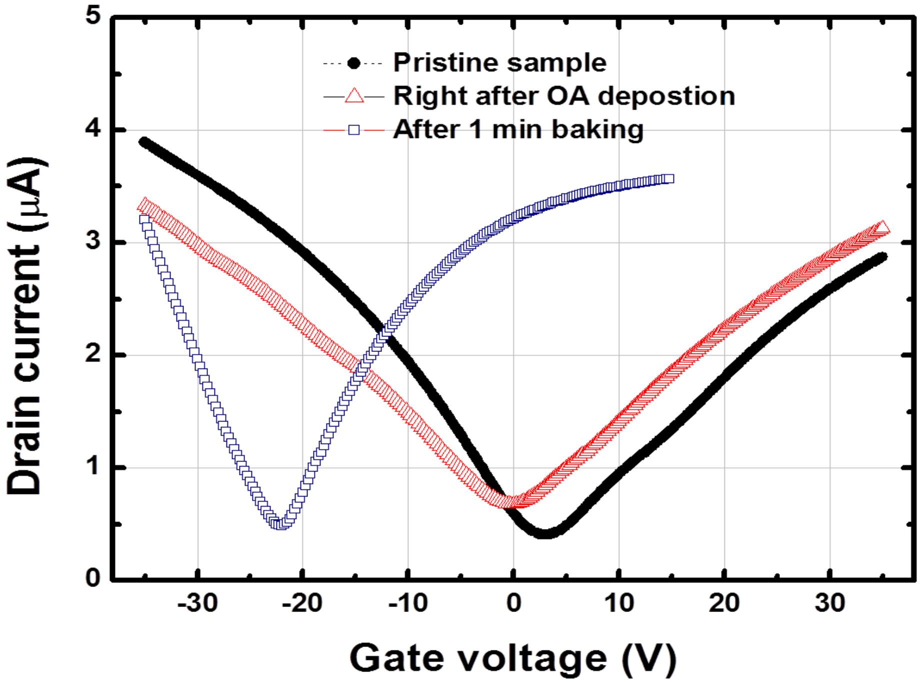

Figure S5. The effect of baking on the hotplate (90 °C) after the deposition of OA molecules by spin casting.

We noticed that the drying step (heating on hot plate or ultra-high vacuum treatment) is necessary in order to trigger OA-graphene electronic interaction. Figure S5 shows pristine device I_D-V_G curve (black curve); the I_D-V_G curve measured right after OA deposition (red curve) exhibits rather weak interaction between graphene and OA: the shift of V_{NP} is only ΔV_{NP}=2.75V. Another measurement taken after a short baking step shows dramatic shift of V_{NP} towards negative V_G values (blue curve). We believe this drying step not only facilitates solvent evaporation but also helps to eliminate water accumulation on graphene, thus minimizing the p-doping effect from moisture.

Monitoring the doping levels by Raman scattering spectroscopy

To investigate the influence of oleylamine on Raman spectra of graphene we employed a single layer graphene field effect (FET) transistor that was subjected to electrical and Raman spectra measurements before and after the OA deposition. The 1.0×10^{-5} M OA solution has been used. The transfer curves of the device are shown in Figure S6(A). Pristine sample shows very weak p-doping as expected, while the effect of OA is clearly seen by the strong shift of V_{NP} to the negative voltages. It yields a doping level of $n=3.1\times10^{12}$cm^{-2}.

Raman spectroscopy is a powerful, non-contact and non-destructive technique. For the case of graphene, Raman spectrum has three prominent features: G-peak (the stretching mode), D-peak (the breathing mode) and the 2D-peak (double resonance of D)[1]. The Raman spectra were characterized by means of conventional confocal micro-Raman spectrometer (HORIBA Jobin Yvon LabRam 800). The excitation 532nm DPSS laser was focused into a spot with a diameter of 0.7μm and safe enough[2] power density of 30kW/cm^2. Raman spectra taken from the center of graphene FET channel before and after OA treatment are shown in the Figure S6B (blue curve). The high intensity and monotonic Lorentzian shape of 2D peak are confirming the single-layer nature of graphene[1]. The D-peak is not seen in the spectra and that fact confirms the good quality of the material. Moreover, D-peak does not appear after the OA deposition and thus, confirms the non-destructive nature of the proposed OA-deposition method. The effect of doping is clearly seen from G-peak stiffening and a decrease of its linewidth after OA deposition (Figure S6B, red curve). Additionally, the intensity of 2D-peak or, more precisely, the intensity ratio I(2D)/I(G) decreased dramatically. The averaged quantities, extracted from three different Raman spectra measured along the channel before and after OA treatment, are shown in Figure S6C. These changes are connected to the increase of the carrier concentration in graphene and were widely discussed in the literature [3–5]. The doping levels estimated from the G-peak position (1585.74 ± 0.76cm^{-1}) and its linewidth (8.33 ± 0.39cm^{-1}) according to the refs. [4, 6] are good in agreement with the result obtained from FET transfer curve (Figure S6A).

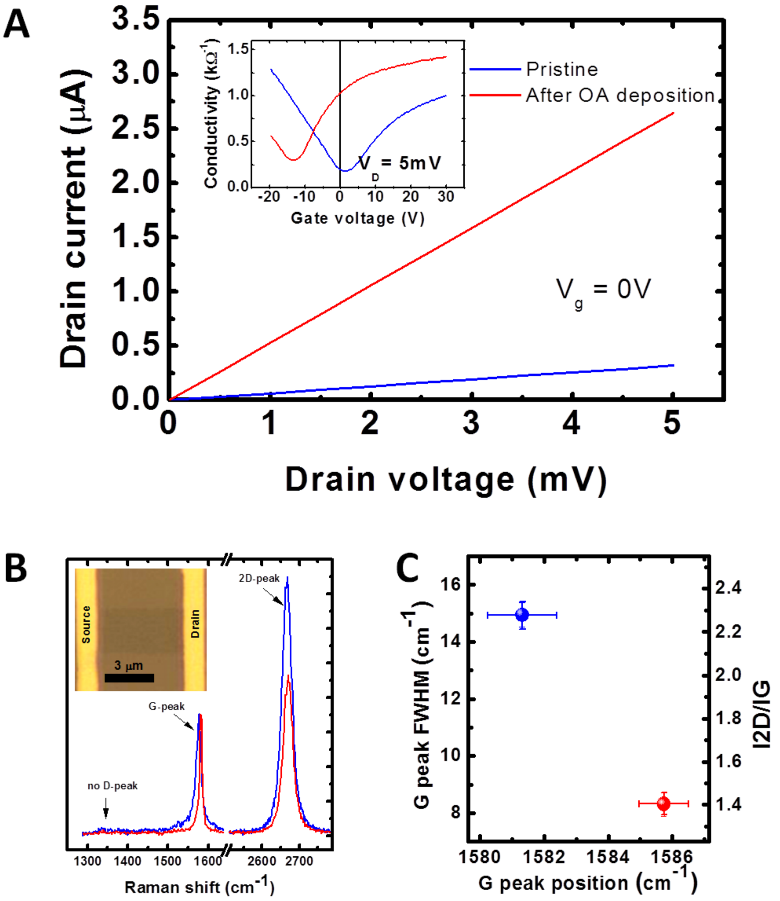

Figure S6. Electrical and Raman spectra measured before (blue line/circle) and after OA treatment (red line/circle) on graphene FET: A) output curves and transfer curves (insert) of the transistor; B) Raman spectra taken in the center of the FET channel; the inset shows optical micrograph of the graphene FET; C) The FWHM and intensity ratio of 2D/G plotted vs. position of the G-peak data averaged over three measurements along the FET channel.

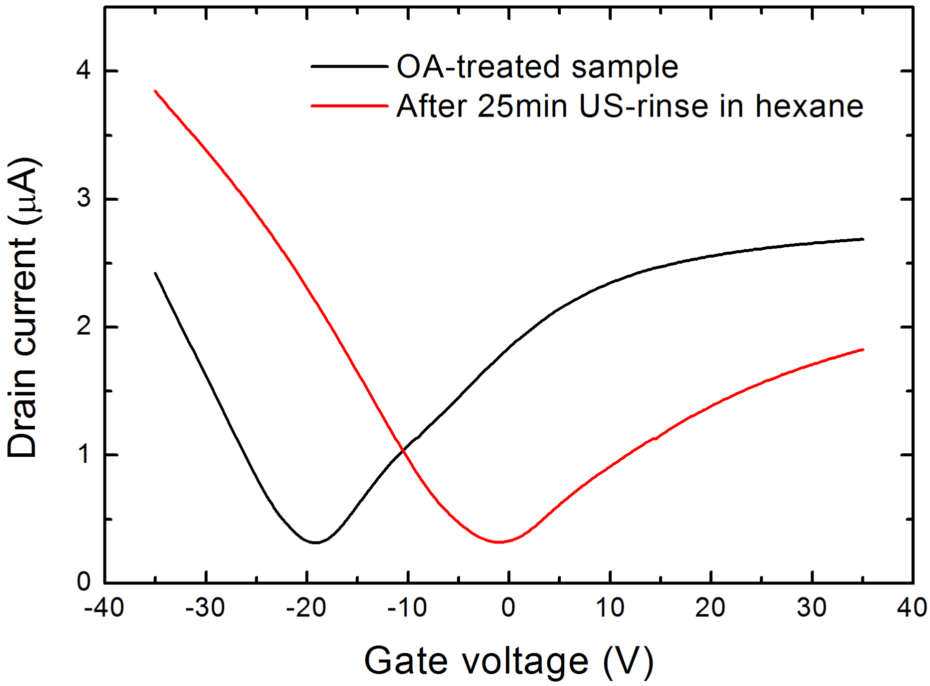

Figure S7. Another OA-treated graphene FET sample characterized before and after OA removal (25 min low power ultrasonication in hexane).

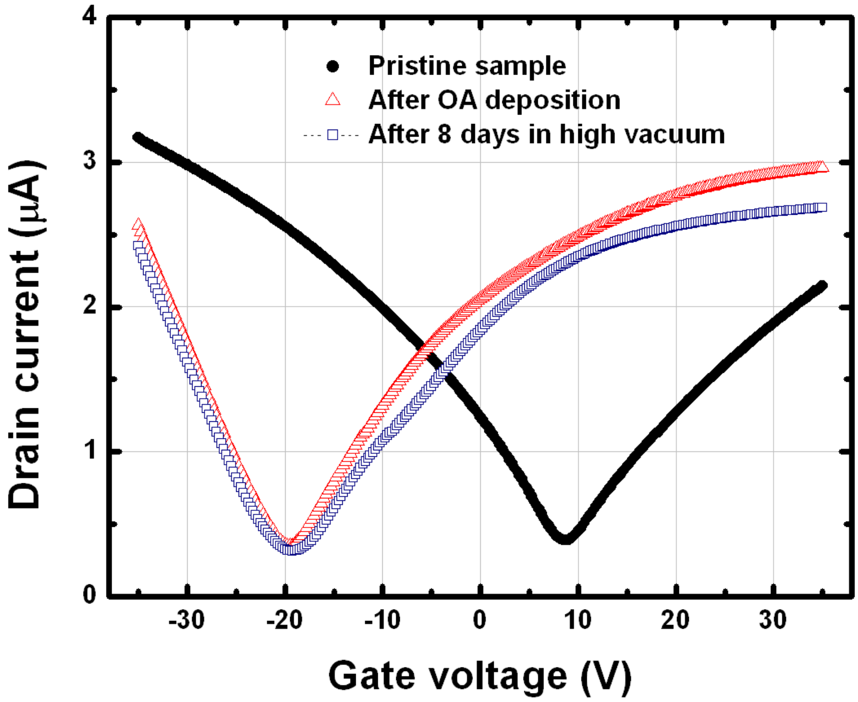

Figure S8. Another OA-treated graphene FET sample characterized before and after extended exposure to high vacuum conditions.

References

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