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ELECTRONIC SUPPLEMENTARY INFORMATION:
Decorating graphene with size-selected few-atom clusters: A novel approach to investigate graphene-adparticle interactions

Jeroen E. Scheerder,* Thomas Picot,* Nicolas Reckinger,* Tomas Sneyder,* Vyacheslav S. Zharinov,* Jean-François Colomer,* Ewald Janssens* and Joris Van de Vondel*

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* Laboratory of Solid-State Physics and Magnetism, KU Leuven, Celestijnenlaan 200 D, box 2414, BE-3001 Leuven, Belgium.
* Research Group on Carbon Nanostructures (CARBONNAGe), University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium.
1 Notes on the fabrication and electronic characterization of cluster-decorated graphene field-effect transistors

1.1 Details of the graphene FET fabrication

Graphene is grown on copper foil using a Chemical Vapour Deposition (CVD) procedure inside a quartz reactor in a hot-wall furnace, using methane as the carbon source. After the growth, polymethyl methacrylate (PMMA) is spincoated on top of graphene, and the copper foil is subsequently etched in aqueous ammonium persulfate. Finally, the resulting 5 mm × 5 mm PMMA/graphene film is transferred onto the p++ Si/ SiO2 (300 nm) substrate, after which the PMMA is removed using acetone.

The optical contrast of the p++ Si/SiO2/graphene stack is employed to identify the locations with single layer graphene without any macroscopic defects. Subsequently, electron beam lithography (EBL) with a customized EBL system from Raith GmbH is performed to define markers and contact structures using a double layer resist mask (PMMA/MA 33%, 4% solid content in methoxy propanol solvent + PMMA 950K, 3.5% solid content in ethyl lactate solvent, 180 nm + 150 nm). After that, a titanium adhesion layer (5 nm) and gold (30 nm) is evaporated with a molecular beam epitaxy system at evaporation speeds of 1 Å·s⁻¹ and 0.23 Å·s⁻¹ respectively. A second lithographic mask is defined using the same EBL system in a single layer resist mask (PMMA 950K, 3.5% solid content in ethyl lactate solvent, 150 nm) followed by a reactive ion etching process using oxygen plasma (200 mTorr, 10 sccm O₂, 300 W, 90 V DC acceleration, 10 s), in order to define the graphene transport bridge. After each lithography step, a lift-off process using acetone is performed.

1.2 Details of the electronic transport measurements and analysis

![Diagram of a four-terminal measurement circuit](image)

**Fig. S1** Overview of the electronic transport measurements. a) Schematic representation of the four-terminal measurement circuit, where a backgate \( V_g \) is applied between the sample and the p++ Si electrode. A DC-current \( I \) is applied, while the voltage \( V \) is measured during the gate sweep. b) \( \sigma \), in function of \( V_g \) (bottom axis) and the induced carrier density \( n_{ind} \) (top axis). The charge neutrality point \( V_{CNP} = 1 \) V is indicated. The electron and hole mobilities can be estimated by linear fits to their respective slope. The insets show graphene’s dispersion relation, where the shaded areas represent the level filling.

Measurements of the field-effect were carried out using a four-terminal geometry (figure S1a) at room temperature in the deposition chamber of the cluster setup. All measurements were performed using a DC current of \( I = 1 \mu A \) (Keithley model 2400 or 6221) and by measuring the voltage drop \( V \) (using the Keithley model 2182A) as a function of the electrostatic gate voltage \( V_g \) (Keithley model 2400). The gate voltage was limited to the experimentally determined range of ±83 V in order to prevent electrostatic breakdown of the SiO₂ dielectric. In figure S1b is shown the sheet
conductance $\sigma = \frac{L}{V}$ for a representable GFET, with $L$ and $W$ the length and width of the transport channel, respectively. The insets represent graphene’s dispersion relation. The top of the shaded region, showing the level filling, corresponds to the chemical potential. By increasing (decreasing) the gate voltage $V_g$, electrons (holes) will be added to the graphene flake which increases (lowers) the chemical potential. The location of the charge neutrality point, $V_{CNP} = 1$ V, suggests the presence of an unintentional extrinsic source of charge carriers, which causes a mild p-doping.

The electrostatically induced carrier density $n_{ind}(V_g)$ depends on the details of the dielectric ($\text{SiO}_2$), and can be determined as $n_{ind} = n_{ind,e} - n_{ind,h} = \varepsilon_0 \varepsilon_r |(\varepsilon|d| |(V_g - V_{CNP})|$, with $\varepsilon_0$ the vacuum permittivity, $\varepsilon_r = 3.9$ the dielectric constant of SiO$_2$, $\varepsilon$ the fundamental charge and $d = 300$ nm the oxide thickness. Note that using this convention, negative values of $n_{ind}$ corresponds to a net hole carrier density.

Three distinct regions can be identified on either the electron or hole side in the $\sigma_e(V_g)$ curve in figure S1b: (i) saturation behaviour towards $\sigma_{e,\text{min}} = \sigma_e(V_{\text{CNP}})$ for $V_g \lesssim |3|$ V, and (ii) a linear behaviour ($V_g \sim |3|$ V - |35| V) which becomes distinctively (iii) sublinear at higher $V_g$ (at $V_g \gtrsim |35|$ V). In region (i), transport is governed by residual carriers $n_{ext}$, the so-called electron-hole puddles, which are present even when $n_{ind}(V_g)$ approaches zero. In the linear region (ii), $n_{ind} \gg n_{ext}$, the main carrier scattering mechanism is governed by long-range Coulomb scatterers and a single scattering time. In this region, the Drude model $\sigma_e = n_{ind}\mu_{e,h}$ can be invoked to extract the carrier-independent electron and hole mobility $\mu_{e,h}$, as is shown by the fits in figure S1b. For the fit procedure, an interval of $\pm 1$ V is taken around the steepest part of the slope $|d\sigma_e/dV_g|_{\text{max}}$. In the third region (iii) the $\sigma_e(V_g)$ relation becomes sub-linear, which can be attributed to competing scattering mechanisms, and the fit to the Drude model (which contains only a single characteristic scattering time) will fail in this region. Models exist to capture the behaviour in all three regions (i-iii) and yield similar results. Both for convenience and the fact that similar adparticle-graphene studies employ the same method, the linear Drude model fit in region (ii) is used to extract the mobility.

### 1.3 Targeted cluster deposition and the deposited density

By inspecting in total 23 depositions on several devices, a mean ratio of $\frac{I_{\text{sample}}}{I_B} \left| \frac{\text{avg}}{\text{avg}} \right. = 21\%$ was obtained with a sample standard deviation of 5%, and hence sample standard deviation on the mean $5% / \sqrt{23} \approx 1\%$, with $I_B$ the beam current, measured by the beam probe prior to the deposition, and $I_{\text{sample}}$ the average beam currents measured on the sample during the deposition. This statistical sample contains depositions with several different types of clusters, beam currents $I_B$ ranging from 23 to 780 pA and sample currents from 4 to 210 pA.

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* For the example in figure S1b, we estimate $n_{ext} \approx 2 \times 10^{11}$ cm$^{-2}$, based on a full fit of $\sigma_e(V_g)$. Furthermore, using Adam et al’s theory, we can estimate $n_{ext} = 5 \times 10^{15} \text{cm}^{-2} \cdot \frac{V_{\text{avg}}}{V} \approx 9 \times 10^{11}$ cm$^{-2}$.

† For lower mobility samples ($\mu_{\text{h,ext}} \lesssim 10^3$ cm$^2$/Vs), for instance for a GFET with a significant amount of adparticles, the long-range scattering mechanism might dominate over the whole experimental $V_g$ range and obscure a sublinear region (iii), which complicates it to employ an identical all-region (i-iii) fit procedure for both GFETs with low and high adparticle density ($\mu_{\text{h,ext}} \gtrsim$ and $\lesssim 10^3$ cm$^2$/Vs, respectively).

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Fig. S2 Aiming the cluster beam. Left panel: Optical image made through the telescope, where a GFET is visible in the deposition chamber, through the aperture (diameter 1.5 mm). Middle panel: GDSII design including the GFET and the aperture, used to calculate the ratio of the sample’s surface with respect to the beam spotsize. Right panel: graphene transport bridge design.
The ratio \( \frac{I_{\text{sample}}}{I_B} = 21\% \pm 5\% (\pm 1\%) \) can be related to the ratio of the conductive surface of the GFET to the cluster beam’s spotsize. Indeed, while the current measurement on the beam probe \( I_B \) captures the full cluster beam, a significant part of the beam will not reach the conductive parts of the device during deposition on a GFET, and hence are not included in the measured \( I_{\text{sample}} \). Using the design of both the deposition chamber apertures and the GFET itself (as shown in figure S2), the surface area of the beam spotsize is estimated to be \( A_{\text{spot}} = 1.76 \text{ mm}^2 \) and the sample area (including wirebonds) \( A_{\text{sample}} = 0.30 \text{ mm}^2 \), hence \( \frac{A_{\text{sample}}}{A_{\text{spot}}} = 17\% \). The surface area ratio accounts for the major part of the discrepancy between \( I_B \) and \( I_{\text{sample}} \). The fact that \( \frac{I_{\text{sample}}}{I_B} \) is slightly but systematically higher than \( \frac{A_{\text{sample}}}{A_{\text{spot}}} \) could be attributed to electrostatic focussing effects. Because of the appreciably good agreement between \( \frac{I_{\text{sample}}}{I_B} \) and \( \frac{A_{\text{sample}}}{A_{\text{spot}}} \), one can employ the estimation \( \phi \approx 3.5 \cdot 10^8 \) clusters/(cm\(^2\)·s) per pA as a rather good approximation to calculate the deposited density \( n_c \). However, as discussed in the main text, the integrated sample current during deposition \( I_{\text{sample}}(t) \) is used as more accurate determination of \( n_c \) after the deposition, since this also takes into account changes in the beam flux during the deposition.


2 Notes on the venting procedure

2.1 Energy of the Ar$^+$ beam and the Au$^{2+}$ ions

In figure S3 are shown the energy characteristics of the Au$^{2+}$ and Ar$^+$ beams that were used in the experiments presented in figure 3. Figure S3a is a reproduction of figure 1c in the main text. The Au$^{2+}$ and Ar$^+$ beams have a similar particle flux at $V_B = 0$: $\sim 250 \text{ pA}$ and $\sim 235 \text{ pA}$ for Au$^{2+}$ and Ar$^+$, respectively. The $dI_B/dV_B$ characteristics have maxima at $V_B = 13 \text{ V}$ and $V_B = 10 \text{ V}$, from which we estimate an average ion energy of $E = 13 \text{ eV}$ and $E = 10 \text{ eV}$ for Au$^{2+}$ and Ar$^+$, respectively. Furthermore, the deposition times were 610 s and 850 s for Au$^{2+}$ and Ar$^+$, respectively. Hence we conclude that flux, energy and the deposited density are similar, which is in favour of the direct comparison as is done in figure 3 in the main text.

![Fig. S3 Energy characteristics for the beam of ions used in the experiments shown in figure 3 of the main text. a) Au$^{2+}$ and b) Ar$^+$.](image)

2.2 Notes on the relaxation behaviour

In figure S4a are shown the $R_s(V_s)$ dependence of a GFET before and after exposure to Ar$^+$ ($5 \text{ eV}$, $n_c = 6.6 \cdot 10^{13} \text{ Ar}^+/\text{cm}^2$), and after venting this device. Note that this deposition was carried out on a different device than the one used in the experiments described in figure 3b in the main text. The difference in CNP and hole mobility after venting versus before deposition are $dN_{CNP} = (0.0 \pm 3.1) \text{ V}$ and $d\mu_h = -(0.1 \pm 0.1) \text{ cm}^2/(\text{Vs})$ respectively. Hence, there is no net change in transport characteristics as is expected since Ar is chemically inert. As discussed in the main text, after exposing the GFET to ionic particles, the induced doping and scattering present a relaxation behaviour. This is further illustrated in figure S4b, where the time dependence of $V_{CNP}$ and $\mu_h$ is given for the ‘after deposition’ state of the GFET. The monotonous trend clearly indicates that both $V_{CNP}$ and $\mu_h$ increase as a function of time and hence that the induced doping and scattering decrease. This further supports the interpretation that, after exposure to ionic particles, charges get trapped near the graphene flake and act as charged impurity scatterers. These charges neutralize, giving rise to the shown relaxation behaviour. To speed up this neutralization process, inherently slow in the high vacuum surroundings, a venting procedure is employed.

![Fig. S4a] and [Fig. S4b] Energy characteristics of the Au$^{2+}$ and Ar$^+$ beams.
Fig. S4 Relaxation behaviour after exposure of the GFET to ionic particles. a) \( R_s(V_g) \) characteristic of a GFET before and after deposition with \( \text{Ar}^+ \) \( (n_c = 6.6 \cdot 10^{13} \text{ Ar}^+/\text{cm}^2) \) and after venting of the device. The black arrow indicates the trend. The inset is a zoom of the data near the CNP, in order to resolve the minimal difference between the data before deposition and after venting. b) Time dependence of \( V_{\text{CNP}} \) and hole mobility \( \mu_h \) for the ‘after deposition’ state of the device in the high vacuum environment. The lines are guides to the eye.

2.3 Notes on the reproducibility of the venting procedure

Adsorbed atmospheric gasses have an impact on graphene’s transport properties, mostly in the form of doping, see e.g. Ref. 7. When the samples are re-evacuated at the end of each venting procedure, degassing of the devices occurs and hence the doping due to adsorbed atmospheric gasses will gradually be neutralized. In order to take into account this gradual neutralization, data which is compared (for instance doping or scattering in function of \( n_c \), such as in figure 4 of the main text) is always generated at the same deposition chamber pressure. However, due to the stochastic nature of the degassing process, still some spread remains on the measured transport characteristics. This is illustrated in figure S5, where \( R_s(V_g) \) is shown for a device with \( n_c = 32 \cdot 10^{13} \text{ Au}_3 \) clusters/\text{cm}^2, recorded at \( P \approx 3 \cdot 10^{-8} \text{ mbar} \) for two subsequent venting cycles (i.e., there was no cluster deposition in between). In this example, the difference between the CNPs is \( dV_{\text{CNP}} = 3 \text{ V} \). Since the venting procedure is an indispensable step of our approach, this stochastic spread on the extracted transport characteristics has to be taken considered in the uncertainty ranges, as is discussed below.
3 Justification of the error bars

3.1 Error on $V_{CNP}$

Since the charge neutrality point voltage $V_{CNP}$ can be readily identified in the FET measurements, the systematic error $\Delta_{sys}V_{CNP}$ is given by the experimental stepsize in $V_g$ which was taken as 0.5 V, which gives the boundaries of the 100% confidence limits in terms of the systematic error.

As discussed above in section 2.3, the venting procedure, an obligatory step in our experiment, results in a certain spread on the CNP. In order to estimate this statistical error, multiple venting cycles were performed immediately after one another (i.e. for a same deposited density of clusters, we performed subsequent venting cycles). In total, we determined the difference in CNP, $dV_{CNP}$, for 23 pairs of FET measurements (1 pair consists for instance of two curves measured at the same pressure for two different venting routines, of which one example is shown in figure S5). Two different samples with a different mobility (i.e. amount of deposited clusters) are considered.

The standard deviation for this sampling was 3.1 V. In other words, this means that for a random pair of FET measurements, $dV_{CNP}$ has a probability of $\sim 68\%$ to be within 3.1 V on either side of the expectation value of the difference which we assume to be equal to zero, that is $dV_{CNP,true} = 0$ V. From this observation, we can estimate the statistical error $\Delta_sV_{CNP}$ on a single FET measurement, by employing error propagation analysis and the result that difference of a pair of $V_{CNP}$ should result in a combined error of $\sim 3.1$ V. This means:

$$3.1 \, \text{V} = \sqrt{\Delta_sV_{CNP,1}^2 + \Delta_sV_{CNP,2}^2}$$

and thus, since we assume $\Delta_sV_{CNP,1} = \Delta_sV_{CNP,2}$,

$$\Delta_sV_{CNP} = \frac{3.1 \, \text{V}}{\sqrt{2}} = 2.2 \, \text{V}$$

In order to now take into account both the systematic and statistical error to come to an overall error on $V_{CNP}$:

$$\Delta V_{CNP} = \sqrt{\frac{\Delta_{sys}V_{CNP}^2}{2^2} + \Delta_sV_{CNP}^2} \approx 2.2 \, \text{V}$$

Note that the systematic error was divided by a factor 2 in order to obtain an estimation for the 68% confidence limits. Hence, for the error on $V_{CNP}$, we take the constant value of 2.2 V, hence $V_{CNP} \pm \Delta V_{CNP} = V_{CNP} \pm 2.2$ V, where $\Delta V_{CNP}$ denotes the boundaries of the 68% confidence limits. The statistical error emerging from the venting procedure dominates clearly.

Fig. S5 Field-effect characteristics $R_s(V_g)$ after two subsequent venting cycles ‘Vent 1’ and ‘Vent 2’ (pressure deposition chamber $P \approx 3 \cdot 10^{-8}$ mbar). The difference between their respective $V_{CNP}$ is 3 V.
3.2 Error on retrieved mobilities

The mobilities are retrieved from a least-squares fit to the data based on the Drude model $\mu_{\text{fit}}$ as described in section 1.2 using a trust-region algorithm. The 95% confidence limits $\Delta_{\text{fit}}\mu_{\text{fit}}$ resulting from this approach are such that $\Delta_{\text{fit}}\mu_{\text{fit}}/\mu_{\text{fit}} \lesssim 2\%$.

Using the same reasoning as made above for the error on the CNP, we determined the standard deviation on difference between the fitted mobility values for pairs of peaks from different sets of venting data to be $104 \text{ cm}^2/(\text{Vs})$. In order to estimate the statistical error on a single mobility value, we find using a similar approach than above, that:

$$\Delta \mu_{\text{fit}} = \frac{104}{\sqrt{2}} \text{ cm}^2/(\text{Vs}) = 74 \text{ cm}^2/(\text{Vs})$$

We can now combine both the errors determined by the fit and the one emerging from the spread due to venting:

$$\Delta \mu_{\text{fit}} = \sqrt{(74 \text{ cm}^2/(\text{Vs}))^2 + (0.01 \cdot \mu_{\text{fit}})^2}$$

Note that we divided $\Delta_{\text{fit}}\mu_{\text{fit}}$ by a factor of 2 in order to give $\Delta \mu_{\text{fit}}$ the interpretation of the estimated limits of the 68% confidence interval.

References