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Originally published:

April 2017

Nano Letters 17(2017)5, 3105-3112

DOI: <https://doi.org/10.1021/acs.nanolett.7b00550>

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Journal:	<i>Nano Letters</i>
Manuscript ID	nl-2017-00550h.R1
Manuscript Type:	Communication
Date Submitted by the Author:	10-Apr-2017
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Abstract

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3 Our scanning tunneling microscopy and X-ray photoelectron spectroscopy exper-
4 iments along with first-principles calculations uncover the rich phenomenology and
5 enable a coherent understanding of carbon vapor interaction with graphene on Ir(111).
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7 At high temperatures, carbon vapor not only permeates to the metal surface, but also
8 densifies the graphene cover. Thereby, in addition to underlayer graphene growth,
9 upon cool down also severe wrinkling of the densified graphene cover is observed. In
10 contrast, at low temperatures the adsorbed carbon largely remains on top and self-
11 organizes into a regular array of fullerene-like, thermally highly stable clusters that are
12 covalently bonded to the underlying graphene sheet. Thus a new type of predominantly
13 sp^2 -hybridized nanostructured and ultrathin carbon material emerges, which may be
14 useful to encage or stably bind metal in finely dispersed form.
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26 Keywords

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29 graphene, carbon deposition, bilayer graphene, wrinkle, cluster
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34 Although the investigation of graphene¹ (Gr) and its epitaxial growth² is a prime area
35 of research in physics, chemistry, and materials science, little is known today about the
36 interaction of carbon vapor with Gr at the microscopic level. This is surprising for several
37 reasons.
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41 First, deep insight into the structure and properties of defects in Gr was gained through
42 transmission electron microscopy experiments, where the electron beam was used to create
43 vacancy type defects by atom removal and to induce their transformations.³⁻⁷ Experimental
44 work on the reverse mechanism of defect creation, *i.e.*, the addition of C atoms (or small
45 molecules) is scarce. Only Lehtinen *et al.*⁸ and Robertson *et al.*⁹ investigated a variety of
46 self-interstitial atom configurations under the non-equilibrium conditions of energy transfer
47 and sputtering by impinging energetic electrons.
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Second, the condensation of carbon vapor on a substrate has been investigated as a route for Gr growth,^{10–12} which is of specific interest for catalytically inactive substrates that do not allow the application of the usual chemical vapor phase deposition methods.^{13,14} Surprisingly, condensation of carbon vapor *on* Gr as a substrate has not come into focus. Noteworthy exceptions are the early work of Tontegode and Rut'kov¹⁵ as well as the more recent study of Nie *et al.*,¹⁶ who investigated the high temperature exposure of Gr on Ir(111) to C vapor which yields additional Gr layers. The latter work presents evidence for the second Gr layer to nucleate from below.¹⁶

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Third, as reactive C atoms (or small C molecules) can be expected to bind chemically to Gr at sufficiently low temperature, one could envision C deposition as an intermediate step to subsequent functionalization of Gr or even as a method to create new Gr hybrid materials.

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In this Letter, using scanning tunneling microscopy (STM), density functional theory (DFT), as well as X-ray photoelectron spectroscopy (XPS), we investigate the processes and morphological effects arising from condensation of C vapor on single-crystalline graphene resting on Ir(111) as a function of the substrate temperature. At high temperatures, we find that C atoms not only permeate through the closed Gr sheet, giving rise to the growth of additional Gr layers underneath,^{15,16} but also incorporate and densify the top Gr layer. When Gr is cooled to ambient, the extra incorporated C induces substantial wrinkling. At low temperatures, permeation and incorporation are blocked to good approximation. Instead C clusters *on top* of Gr form, being firmly attached to the Gr sheet. The clusters display a surprisingly regular array. We obtain insights into the structure and the binding of these clusters to graphene and study their transformation through heating.

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Figure 1(a) displays a large-scale STM topograph, which serves as a reference for the evolution of a Gr layer on Ir(111) upon exposure to C vapor at high temperatures. The initial Gr layer is a single crystal sheet grown to complete closure of the metal surface. It is well aligned with the Ir(111) substrate, so that it forms a moiré of 2.5 nm periodicity with Ir(111) (see Methods Section). In the following it is referred to as the Gr cover. The Gr

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3 cover was subsequently exposed to a carbon vapor flux at a sample temperature of 1170 K
4 and for a duration that could have resulted in the formation of 0.8 monolayers (ML) of
5 graphene. We note that the C vapor is composed not only of C monomers, but contains
6 about twice as many C trimers (compare Methods Section). Figure 1(b) is a schematic
7 representation of the resulting topography displayed in Figure 1(a), and it helps to distinguish
8 between mono- (gray) and bilayer (blue) Gr areas. Characteristic features in Figure 1(a)
9 are triangular bilayer islands, mostly with a bright bulge in their center, a wide stripe of
10 bilayer Gr crossing the image and a network of bright lines. All bilayer Gr resulting from C
11 deposition is formed *underneath* the covering Gr sheet, as has been demonstrated by Nie *et*
12 *al.*¹⁶ Under the conditions of preparation used here, Gr underneath grows with precisely the
13 same orientation as the Gr cover. Thereby bilayer areas exhibit an enhanced moiré contrast
14 facilitating their assignment. This can be seen in Figure 1(c) which displays a monolayer area
15 (upper right) next to a bilayer area with enhanced moiré contrast. The arrow in Figure 1(c)
16 highlights the location, where the underlayer island, formed as a result of C vapor exposure,
17 has grown into an Ir step edge. The borderline displays a characteristic sawtooth pattern
18 with moiré periodicity (compare ref. [17]). We note that depending on the conditions, also
19 misoriented Gr grows underneath the cover, then giving rise to additional moirés.¹⁸ The
20 Supporting Information provides an example as Figure S1. Inspection of Figure 1(b) makes
21 plain that the area of bilayer Gr is substantially smaller than an area fraction of 0.8 that
22 one would expect from the deposited amount, consistent with the analysis of several STM
23 topographs. In fact, a substantial fraction of C re-evaporates and is not incorporated into the
24 sample. At deposition temperatures of 1370 K re-evaporation is found to be nearly complete.
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47 Outstanding in Figure 1(a) are the many bright line segments (specifically in the large
48 bilayer stripe) and even more the network of bright lines with three-armed branching points
49 [black in the schematic in Figure 1(b)]. The network extends over the entire topograph and
50 displays a preference to stay close to Ir substrate steps. These bright lines are wrinkles and
51 folds in the Gr cover. As apparent from the profile displayed in Figure 1(d), the wrinkles
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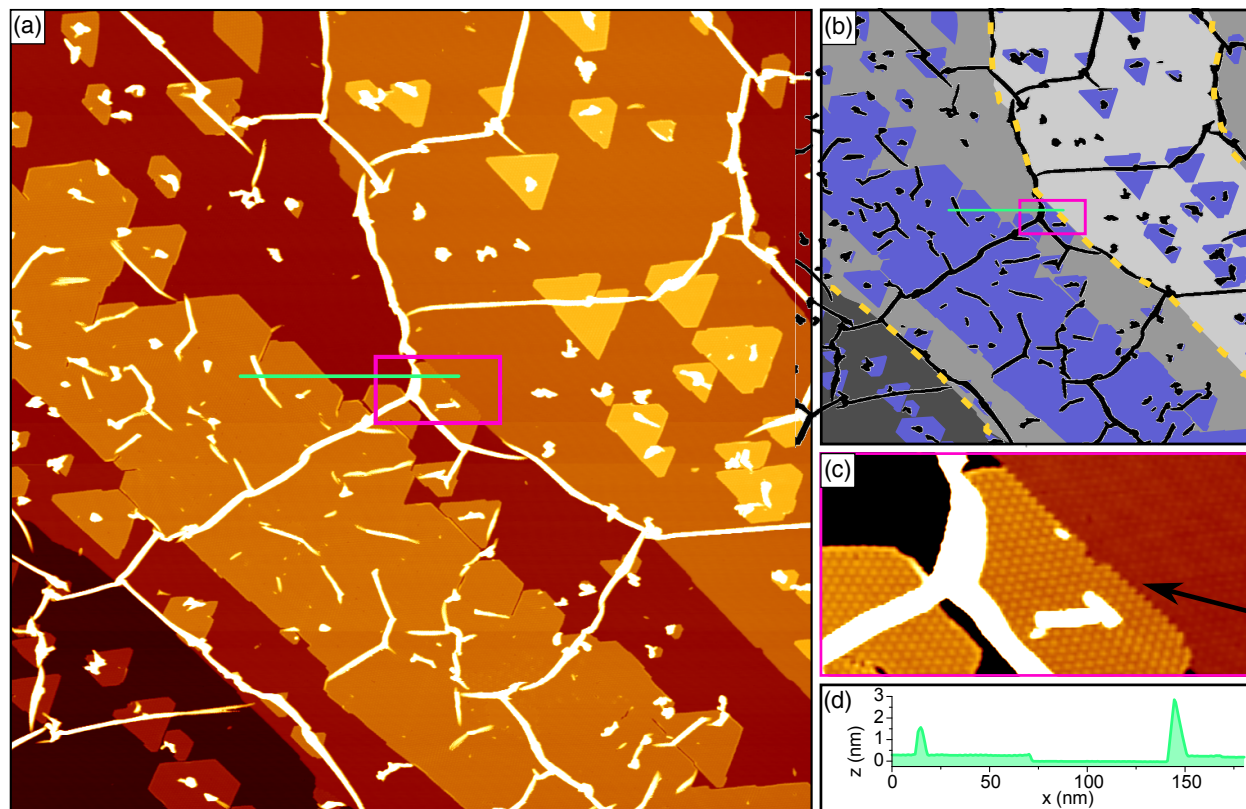


Figure 1: (a) STM topograph of Gr/Ir(111) after deposition of 0.8 ML C at 1170 K. (b) Schematic representation of (a): the position of Ir substrate steps of monatomic height are indicated by yellow dashed lines; the Ir terraces covered by monolayer Gr are shaded gray according to their height (light gray - highest terrace level, dark gray - lowest terrace level), bilayer Gr islands and areas are colored in blue and the position of wrinkles is indicated by black lines. (c) Magnified view of the area indicated in (a) and (b) by a pink box. The arrow indicates where an underlayer Gr island has grown into a preexisting Ir step. (d) Height profile along the green line indicated in (a) and (b). STM topograph sizes are (a) 680 nm \times 680 nm and (c) 107 nm \times 55 nm, respectively.

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3 have a typical height of 2-3 nm. To highlight the significance of the wrinkles we evaluated
4 their three-dimensional topography prior and after C deposition and found that compared
5 to a Gr cover not exposed to C vapor, the additional wrinkles give rise to an extra, folded
6 Gr area of $(0.8 \pm 0.2) \%$.
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11 Even without exposure to C vapor, occasional wrinkles are present in the Gr cover (com-
12 pare Figure S2(a) of the Supporting Information). They originate from different thermal
13 expansion coefficients of Gr and Ir. As the Gr cover is cooled from the high growth tem-
14 perature, Ir shrinks, but Gr does not. Pinned to the substrate, Gr releases the resulting
15 compressive strain partly by wrinkle formation.^{19,20} The wrinkle density and induced extra
16 Gr area are enhanced by more than a factor of three through the high temperature treat-
17 ment of the Gr cover in C vapor (compare Figure S2(b) of the Supporting Information).
18 Our observation therefore forces us to assume that after exposure to a C vapor additional
19 C atoms are incorporated *into* the Gr cover on Ir(111), *i.e.*, after the C vapor treatment Gr
20 is already compressed prior to the cool-down (compare also Figure S2(c) of the Supporting
21 Information). This pre-straining is the origin of the enhanced wrinkling upon cooling.
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33 To understand permeation *through* Gr and incorporation of C vapor *into* the Gr cover,
34 we need to consider the energetics of the processes involved. If we set the energy of a C
35 atom in a perfect Gr sheet on Ir(111) to $E_{\text{Gr}} = 0$ eV, according to our DFT calculations
36 the energy of a C atom in the vapor is $E_{\text{v},1} = 8$ eV, the one of a C atom adsorbed on Gr
37 $E_{\text{on C},1} = 6.4$ eV (the adsorption energy is thus $E_{\text{ads},1} = 1.6$ eV), and the energy of the single
38 C atom adsorbed on Ir(111) is $E_{\text{on Ir},1} = 0.7$ eV²¹ [compare Figure 2]. The corresponding
39 numbers for a trimer are $E_{\text{v},3} = 11$ eV (assuming the trimer binding energy of 13 eV obtained
40 by Raghavachari and Binkley²²), $E_{\text{on C},3} = 9.1$ eV, $E_{\text{ads},3} = 1.9$ eV, and $E_{\text{on Ir},3} = 3$ eV.²¹
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49 These numbers imply an enormous decrease in energy upon permeation of vapor species
50 through the Gr sheet to the Ir(111) surface, providing thereby the driving force for the
51 growth of Gr islands underneath the Gr cover, as has already been pointed with qualitative
52 arguments by Nie *et al.*¹⁶ At the same time, these numbers imply also an even larger drop in
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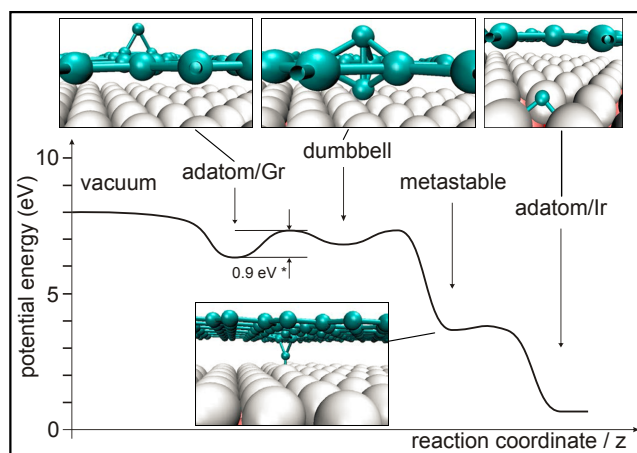


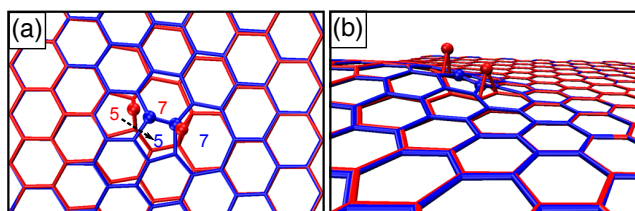
Figure 2: Energy for a carbon atom along a reaction coordinate from the vacuum to Ir(111) based on our DFT calculations. Zero energy corresponds to a C atom in a regular Gr lattice position. The insets display the C atom in the adatom to Gr, dumbbell, metastable, and adatom to Ir positions. The magnitude of the barrier indicated by * is taken from ref. 23.

energy upon incorporation of vapor phase species into regular lattice sites of the Gr cover.

Therefore, disregarding the details of the kinetic processes involved, we propose the following scenario: the C species condense from the supersaturated vapor on the hot Gr cover sheet, where they either re-evaporate (based on the numbers given above and with a pre-exponential factor ν_0 of 10^{12} the residence time τ can be estimated using the Arrhenius law $\frac{1}{\tau} = \nu_0 \cdot e^{-\frac{E_{ads,1}}{k_B \cdot T}}$, and is of the order of 10^{-5} s) or approach one of the two sinks for adsorbed C species: either regular sites in the Gr cover itself, or adsorption sites on Ir(111) in a 2D lattice gas of C species, from which eventually Gr islands nucleate, providing again regular lattice sites. It is important to note that the energy (chemical potential) of a C atom in a regular lattice site of the Gr cover rises due to the buildup of strain upon atom incorporation. Therefore, after some strain buildup, this sink ceases and the Gr cover will expel the same amount of C species to the Ir substrate that it incorporates from the adsorbed C, providing thereby the feed for underlayer Gr growth. This qualitative picture provides not only an explanation for the underlayer Gr growth, as has been observed before,¹⁶ but also for the enhanced wrinkling in consequence of the Gr cover layer compression due to C species incorporation, which has been overlooked so far.

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3 Due to the high sample temperature, the complexity of possible defect arrangements
4 and transformations in Gr, and the presence of not only monomers but also trimers in the
5 vapor, it is currently close to impossible to pinpoint with certainty *the* decisive atomic scale
6 vapor, it is currently close to impossible to pinpoint with certainty *the* decisive atomic scale
7 processes and their barriers for the above scenario. Nevertheless, it is instructive to consider
8 possible candidates.
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13 (i) Dislocation cores in Gr are associated with 5-7 defects, pentagon-heptagon pairs.
14 Where Gr flakes join during the growth process, 5-7 defects are formed to accommodate
15 slight misalignments.¹³ Therefore these defects are always present to some extent in the
16 Gr cover. When two migrating C atoms (migration barrier 0.5 eV²⁴) meet at a 5-7 defect
17 (the dislocation core), according to our *ab initio* calculations they are incorporated into
18 the Gr network without any additional barrier and induce dislocation climb as illustrated
19 in Figures 3(a) and (b). As the dislocation core is not changed upon atom incorporation,
20 but only translated, the processes may be repeated again and again. Nevertheless, it is
21 accompanied by gradual buildup of compressive strain in the Gr cover making incorporation
22 energetically more and more costly. Dislocation climb by incorporation of vacancies, rather
23 than adatoms, has been already been observed in transmission electron microscopy of Gr.^{5,6}
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43 Figure 3: (a) Top and (b) side view of a dislocation core represented by a 5-7 defect before
44 (red) and after (blue) spontaneous incorporation of the two C adatoms (red balls) and the
45 resulting dislocation climb. The dashed arrow indicates the migration of the 5-membered C
46 ring.
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50 (ii) An adsorbed C adatom may reach the dumbbell configuration depicted in the inset
51 of Figure 2 through overcoming a barrier of 0.9 eV.²³ From this metastable state, just 0.4 eV
52 higher in energy than the adatom position (consistent with the result of Ma²³) the atom
53 dives without any noticeable barrier down to the Ir(111) substrate, where it contributes to
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3 the buildup of a C adatom gas. Based on our numbers, the probability of a C atom to reach
4 the dumbbell configuration within its lifespan is appreciable.
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7 (iii) As DFT calculations²⁵ indicate, upon encounter of two migrating C adatoms on the
8 perfect Gr lattice, an inverse Stone-Wales (ISW) defect can spontaneously form, without
9 significant additional barrier and with a large energy gain of about 7 eV. The resulting ISW
10 defect, consisting of two paired pentagons accompanied by two separate heptagons, deforms
11 the Gr lattice substantially. For freestanding Gr, a bulge with a surrounding depression
12 gives rise to a height amplitude of 2.7 Å.²⁵ Assuming a similar deformation for Gr on Ir(111),
13 we can imagine an ISW defect to be the nucleus for incorporation of additional C species,
14 resulting in larger deformations. From there C is expelled to the Ir substrate at the locations,
15 where in consequence of deformation, Gr is pressed close to Ir. Indeed, nearly all triangular
16 Gr islands grown underneath the Gr cover in Figure 1(a) carry in their center a bright bulge
17 in plausible agreement with our speculation. We note that the bright bulges are in this view
18 metastable, and consistent with this notion, do not form anymore for vapor deposition above
19 1300 K. We also remark that earlier transmission electron microscopy studies⁹ suggested
20 significant energy barriers for the formation of ISW defects, which could explain why bulges
21 are not so frequent in the morphology.
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37 Figure 4(a) displays an STM topograph, which serves as a reference for the reaction
38 of a Gr cover on Ir(111) upon exposure to C vapor at low temperatures, close to ambient.
39 At 400 K the sample was exposed to 0.1 ML carbon vapor, an amount corresponding to an
40 average of 21 C atoms per moiré unit cell. Based on the computed adsorption energies
41 of $E_{\text{ads},1} = 1.6$ eV and $E_{\text{ads},3} = 1.9$ eV, re-evaporation must be considered to be absent.
42 Apparently, the deposited C largely remained *on* the Gr cover and was subject to a self-
43 organization process. The resulting clusters are arranged with the moiré periodicity and
44 form an imperfect C cluster lattice. In Figure 4(a) less than 2% of the moiré unit cells
45 are empty, about 5% of the clusters are misplaced on interstitial positions, and few clusters
46 extend over two unit cells. The apparent size of the clusters varies considerably, indicated
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3 by the height variation from 1 Å to 10 Å with an average of 3 Å. This implies a substantial
4 variation of the number of C atoms forming the clusters. The order of the cluster lattice
5 is inferior to the one of lattices formed by Ir, Pt, W, or Rh on Gr/Ir(111), but superior to
6 one of other metals like Fe, Au, Co.²⁶ At 400 K, pronounced cluster lattices are observed for
7 C exposures up to 0.3 ML. For larger amounts the clusters grow too large, and eventually
8 touch or coalesce, whereby loss of order is induced.
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11 The clusters result from diffusion of the deposited C species to locations within the
12 moiré unit cell, where they bind more strongly to the Gr cover and aggregate. For the given
13 deposition rate (see Methods Section), optimum order in the C cluster lattice is achieved in
14 the temperature range from 300 K to 400 K. At 130 K order is lost, due to a lack of C species
15 diffusion, while at 550 K the amount of empty moiré cells is increased, due to enhanced C
16 species diffusion. Based on the analysis in Figure 4 (b), the clusters bind to the hcp-areas in
17 the moiré (as do metal clusters^{26,27}). In an hcp-area, an Ir(111) hcp threefold hollow site is
18 in the center of the Gr C ring; thus three of the C atoms in a ring sit atop of Ir surface atoms.
19 Though after deposition of very small amounts, *e.g.*, 0.03 ML, clusters can be removed by
20 the STM tip, after deposition of 0.1 ML or more, clusters are strongly bound and cannot
21 be manipulated by the STM tip. Their stability allows one to image them with relatively
22 low tunneling resistance, such that molecular orbital resolution is achieved, as displayed in
23 Figure 4 (c). The molecular structure of the clusters as imaged by STM resembles strikingly
24 the one of C₆₀ molecules imaged with a C₆₀ functionalized tip by Lakin *et al.*²⁸ This may be
25 due to sp² C fragments adsorbed to the tip and would imply a predominantly fullerene-like
26 sp² type cluster structure. The cluster motifs of the topograph bear also similarity to STM
27 images of the sp² shell of nanodiamonds as observed by Pawlak *et al.*²⁹
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49 To gain insight into the cluster binding mechanism, we collected XP spectra of Gr/Ir(111)
50 before and after deposition of 0.3 ML C. This amount ensures a strong XPS signal and still
51 results in a well-ordered C cluster array. The bottom panel of Figure 4 (d) displays the sharp
52 C 1s peak prior to C deposition at a binding energy (BE) of 248.1 eV and an experimental
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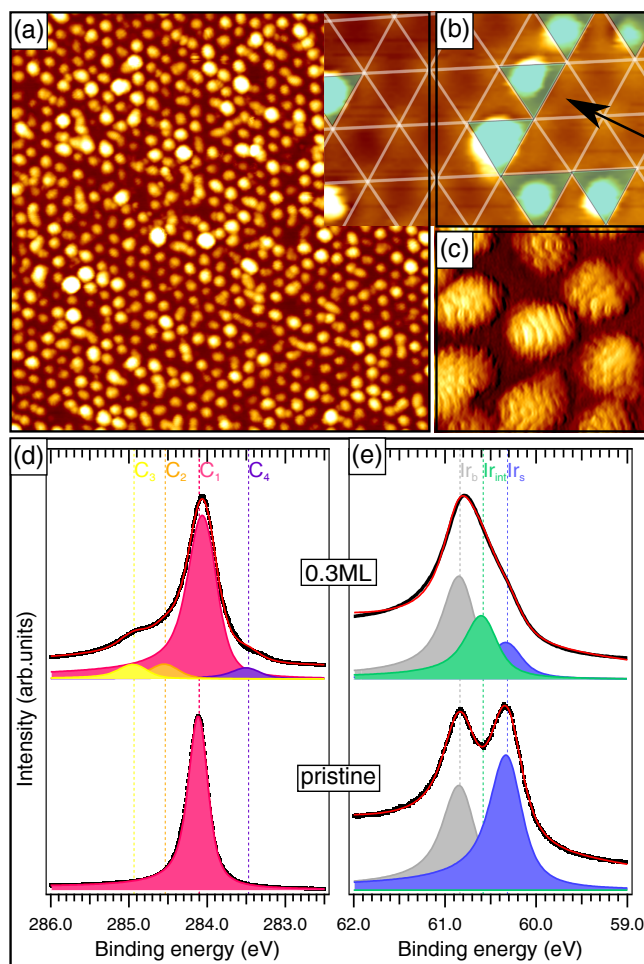


Figure 4: (a) STM topograph of the C cluster lattice on Gr/Ir(111) after exposure to 0.1 ML C vapor at 400 K. Image size is 60 nm \times 60 nm. (b) STM topograph after exposure of Gr/Ir(111) to 0.03 ML C vapor at 400 K. The only partly occupied moiré allows one to draw a hexagonal network connecting the bright top-areas (in these areas an Ir atop site is located in the center of a C ring, compare ref. 27). The clusters are positioned in down-pointing triangles of the network. Together with the known crystal orientation (the $[\bar{1}\bar{1}2]$ -direction is indicated), this implies cluster adsorption in the hcp-areas of the moiré. Image size is 8.5 nm \times 8.5 nm. (c) STM topograph after 0.1 ML C deposition on Gr/Ir(111) at 400 K with molecular orbital cluster resolution obtained by imaging with relatively low tunneling resistance; $U_s = 1.5$ V, $I_t = 0.6$ nA. Image size is 7.5 nm \times 7.5 nm. (d) XP spectra of the C 1s peak of pristine Gr/Ir(111) (lower spectrum) and after additional 0.3 ML C deposition (upper panel) fitted with four components (see text). (e) Ir 4f_{7/2} spectra of pristine Gr/Ir(111) (lower panel) and after additional 0.3 ML C deposition (upper panel). The spectra display the bulk peak Ir_b, the surface peak Ir_s, and an additional component Ir_{int}, due to chemical interaction after C deposition (see text).

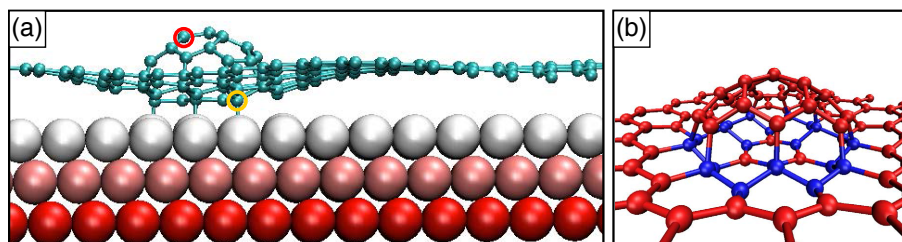


Figure 5: (a) Side view for the DFT-optimized geometry of a 19 C atom cluster in the hcp-area of Gr/Ir(111). Encircled are a C atom of the cluster (red) and a C atom of the rehybridized area underneath the cluster (yellow). See text. (b) Perspective view of the same system as in (a), but with the C atoms colored according to their coordination: red for 3 neighbors (counting bonds to Ir atoms) and blue for 4 neighbors. Ir substrate atoms are not shown for clarity.

Gaussian full width at half maximum (GFWHM) of 0.21 eV. It is well reproduced through a single fit component C_1 (magenta), in agreement with previous work.³⁰ After C deposition, the predominant intensity of the C 1s peak is still reproduced by a broadened (GFWHM of 0.37 eV) and slightly shifted (-0.1 eV) C_1 component [upper panel in Figure 4(d)]. We attribute these changes to variations in the chemical environment and doping of the sp^2 hybridized Gr atoms.

Moreover, the experimental spectrum displays a high-energy shoulder. Diamond-like sp^3 carbon is characterized by a C 1s component in the range of 284.9 eV³¹ to 285.2 eV³² roughly matching the position of the high-energy shoulder. At the same time, a similar shoulder (“rehybridization shoulder”) has previously been observed after metal cluster adsorption on Gr/Ir(111) and was attributed to Gr atoms rehybridized underneath and in the vicinity of the metal clusters to sp^3 carbon.^{30,33} In principle both effects could contribute to the formation of this shoulder, and their origin will be reanalyzed below with additional information. To adequately fit the high-energy shoulder, two additional components C_2 (orange) and C_3 (yellow) must be introduced, similar to the rehybridization shoulder.³⁰

Finally, also towards the low-energy side the experimental spectrum develops a tiny shoulder accounted for in the fit through a component C_4 (purple) at a BE of 283.45 eV. This shoulder is absent in the C 1s spectrum after metal cluster growth. We interpret

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3 this component to be due to carbidic carbon, *i.e.*, carbon chemisorbed to Ir.³⁴ After ion
4 irradiation of Gr/Ir(111), creating detached C atoms, a similar intensity increase at the low
5 binding energy side is observed, consistent with our assignment. The component C₄ thus
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9 seems to indicate that a small amount of carbon – presumably monomers – permeated the
10 Gr sheet even at 400 K deposition temperature, *e.g.*, by mechanism (ii) mentioned above.
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13 The Ir 4f_{7/2} spectrum of pristine Gr/Ir(111) displayed as the bottom panel in Figure 4 (e)
14 features two components. The component at a BE of 60.8 eV is assigned to Ir bulk atoms (Ir_b)
15 whereas the component at a BE of 60.3 eV originates from the surface atoms (Ir_s) consistent
16 with literature.³⁵ Upon C deposition the surface component Ir_s is strongly reduced [upper
17 panel of Figure 4 (e)] and a third component Ir_{int} at a BE of 60.5 eV has to be introduced for
18 a reasonable fit. The Ir_{int} component must be attributed to Ir surface atoms now interacting
19 chemically with the C. The large spectral weight of the Ir_{int} component suggests that it is
20 made up of Ir atoms binding to rehybridized C atoms and Ir atoms bound to permeated C
21 monomers.
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31 DFT calculations, though unable to explore the configuration space to any reasonable
32 extent, are nevertheless instructive to understand the link between cluster binding and cluster
33 structure. First we joined 16 and 58 atom clusters of sp³ diamond to the hcp-areas. After
34 relaxation the energies per C atom were 2.0 eV and 1.33 eV, respectively. For 10 and 19
35 atom clusters consisting of sp² hybridized flakes that were joined as hemispherical caps to
36 Gr/Ir(111) in the hcp-areas, the energies per C atom were 1.6 eV and 1.0 eV, respectively,
37 much lower as for the diamond clusters of comparable size. Figure 5 (a) displays a side view
38 of the 19 atom cluster forming a fullerene type hemispherical cap on the Gr cover. It is
39 apparent that the Gr sheet bends down towards the substrate at the cluster location. This
40 is enabled in the hcp-areas with Gr C atoms sitting atop of Ir atoms. There C(2p_z) orbitals
41 hybridize with the Ir(5d<sub>3z²-r²) orbitals and form chemical bonds.³⁶ In the perspective view
42 of Figure 5 (b) the threefold coordinated sp² type C atoms are colored red, while the fourfold
43 coordinated sp³ hybridized C atoms (including bonds to the Ir substrate not shown) are
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3 colored blue. Results for the other cluster sizes are provided as Figure S3 in the Supporting
4 Information. Based on its low energy, we are convinced that the 19 atom cluster represented
5 by Figure 5 (a) and (b) is a typical case.
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9 A consistent interpretation of the XP spectra in the light of the DFT calculations is
10 obtained by assuming that (i) the majority of deposited C atoms contributes to the C₁ peak
11 of sp² hybridized carbon (fullerene-type carbon), (ii) some carbon, presumably deposited
12 monomers, still permeate to the Ir substrate giving rise to the C₄ component and contributing
13 through their binding to Ir to Ir_{int}, (iii) rehybridization of C atoms in the Gr cover gives
14 rise to the majority of intensity in the C₂ and C₃ components. Since components C₂ and C₃
15 are still small after deposition of 1 ML C atoms, we rule out that a significant part of the
16 deposited C atoms is sp³ hybridized. Together with the molecular orbital appearance of the
17 clusters, these arguments provide evidence for a fullerene-type hemispherical cap structure
18 of the clusters.
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29 It is not surprising that the deposited C is predominantly present in sp² hybridized form.
30 Surfaces of sp³ bonded diamond reconstruct involving π -bonding,³⁷ driven by the removal
31 of energetically costly dangling bonds. For the same reason, also amorphous carbon films
32 display at their surface predominantly sp² bonding.³⁸ For the present case, we imagine that
33 in the hcp areas, where hybridization is facile, C trimers and C atoms attach. Thereby
34 growth normal to the Gr cover is induced. In order to minimize the system energy, there
35 will be a strong tendency of subsequently arriving C species to reduce the energy associated
36 with the resulting dangling bonds, *i.e.*, to connect different C atoms and atom groups and
37 thereby to remove dangling bonds. This leads directly to sp² bonding motifs resulting in
38 configurations similar to the hemispherical fullerene cap.
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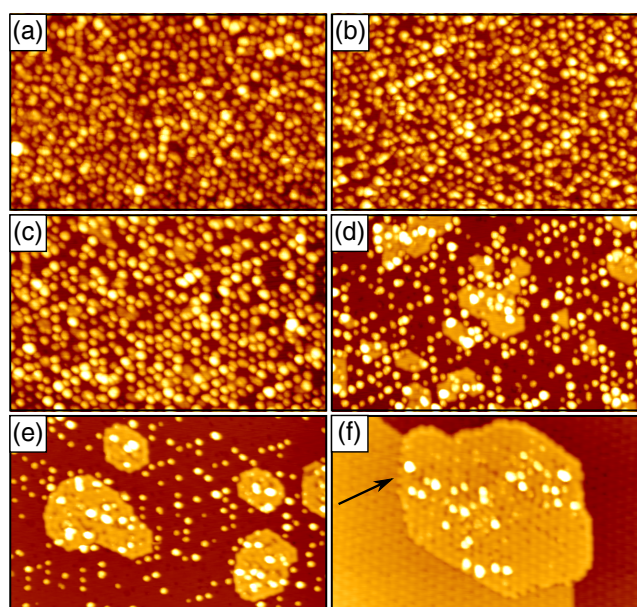
49 Contrary to the interpretation given here, one might propose that the C clusters form
50 *underneath* the Gr sheet. Indeed, in view of the tiny component C₄ a small amount of
51 carbon atoms may have penetrated the Gr cover and be adsorbed to Ir(111), presumably as
52 monomers. However, we rule out that the clusters seen in the STM topographs are grown
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3 underneath the Gr cover for the following reasons: (i) As mentioned above, small clusters
4 can be picked up by the STM tip, providing direct evidence for the formation on top of the
5 Gr sheet. (ii) Considering the average apparent cluster height of 3 Å, formation underneath
6 would imply a large deformation energy in the Gr cover. (iii) Clusters form in the hcp-areas,
7 where the Gr cover has been shown to be most sticky to arriving particles and where it
8 binds strongest to the substrate. Cluster formation underneath would be expected in the
9 top areas, where the Gr does not bind to the substrate³⁶ and provides space for intercalation.
10 (iv) The vast majority of carbon arrives as trimers on the Gr sheet, for which penetration
11 barriers much larger than the 0.9 eV calculated for monomers must be assumed. (v) We will
12 see in the next section that some clusters survive up to annealing temperatures of 1350 K,
13 a temperature at which any C cluster in contact with Ir would have readily transformed to
14 Gr.³⁹

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16 According to our DFT calculations, the C clusters adsorbed on Gr/Ir(111) have energies
17 on the order of 1 eV and are thus metastable configurations with respect to Gr. Annealing
18 is therefore likely to transform the clusters to lower energy configurations, *e.g.*, to Gr.

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20 Figure 6 presents STM results of an annealing sequence, starting (a) after exposure of
21 Gr/Ir(111) to 0.3 ML of C at 400 K, and after isochronal annealing for 60 s to (b) 600 K, (c)
22 800 K, (d) 1000 K, (e) 1200 K, and (f) 1350 K. The filling factor (number of clusters per moiré
23 unit cell) is initially close to 100 %, remains almost constant up to 800 K (90 %), and then
24 decreases gradually with increasing temperature. Four qualitative features are remarkable
25 in the annealing sequence: (1) With increasing annealing temperature there is only cluster
26 disappearance, but no ripening, *i.e.*, there is no growth of some clusters at the expense of
27 others. This is contrary to what is found for metal clusters on Gr/Ir(111) which display
28 a clear ripening through cluster diffusion and coalescence (Smoluchowski ripening).^{26,33} (2)
29 Starting already at 800 K and well visible after annealing to 1000 K, flat platelets of uniform
30 height are visible, which grow in area and decrease in number with increasing annealing
31 temperature. These flat platelets result from underlayer Gr. Their height of 3 Å, the growth
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3 of the platelets into preexisting substrate steps, and the characteristic sawtooth pattern with
4 moiré periodicity of the grown in edge in Figure 6(f) (see arrow) leave no doubt that the
5 majority of clusters transformed into bilayer Gr during heating. (3) It is surprising that
6 some clusters have already disappeared at the lowest annealing temperature, while many
7 others survive up to 1200 K. This broad temperature range of disappearance indicates that
8 the cluster stability strongly depends on the precise cluster configuration. (4) Some clusters
9 remain on bilayer areas. It is no coincidence that in Figure 6(f) the only clusters left are
10 found on the bilayer Gr island.



39 Figure 6: (a) STM topograph of 0.3 ML C deposited on Gr/Ir(111) at 400 K and subsequently
40 annealed to (b) 600 K, (c) 800 K, (d) 1000 K, (e) 1200 K, and (f) 1350 K. Image sizes are
41 80 nm \times 50 nm. The arrow in (f) indicates the characteristic sawtooth pattern with moiré
42 periodicity of the grown in edge.

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46 Our observations may be rationalized by viewing the clusters as not being adsorbed to
47 the Gr cover, but by assuming that the system consists of C clusters adsorbed to the Ir(111)
48 substrate, which are joined by Gr: each adsorbed C aggregate forms with the underlying piece
49 of diamond-like carbon (emerging from local rehybridization of the Gr cover) an inseparable
50 unit. Clusters cannot merge as they are fixed by Gr spacers, *i.e.*, Smoluchowski ripening is
51 prohibited. Detachment and reattachment of C atoms does not take place for C atoms in
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3 the upper part of the cluster [*e.g.*, the C atom encircled red in Figure 5(a)], where it could
4 lead to Ostwald ripening of the clusters, because a C atom detachment would involve an
5 increase of the system energy of the order of 5 eV [compare Figure 2] before the atom could
6 reincorporate. Only for those C atoms already in direct contact with Ir(111) [*e.g.*, the C
7 atom encircled yellow in Figure 5(a)], detachment and hence adsorption on the substrate
8 can take place, as due to the close proximity of the substrate being a low energy sink, a low
9 energy transition state exists. Out of these C atoms the underlayer Gr nucleates and grows
10 until the excess C in the clusters is consumed, such that the cover is eventually restored
11 as a Gr sheet. As the clusters are not all alike, the barriers for C atom detachment to the
12 Ir surface will vary considerably, explaining the broad temperature range of gradual cluster
13 disappearance [observation (3)]. In case underlayer Gr has grown under the Gr cover still
14 containing clusters, the clusters' contact to Ir is lost. Thereby the driving force for C atom
15 detachment is lost, and the cluster decay is prevented [observation (4)]. Since in this case the
16 upper Gr layer is detached from the Ir(111) substrate and can be viewed as quasi-freestanding
17 it must be concluded, that the C cluster stability does not depend on the Ir substrate, *i.e.*,
18 once formed on the Gr cover the clusters will be stable even without the Ir substrate.
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35 In conclusion, our experiments and simulations uncover two new phenomena caused by
36 the interaction of C vapor with Gr on a metal. First, exposure to C vapor at high tem-
37 peratures gives rise to drastically enhanced wrinkling in the Gr cover after cool down. The
38 origin of the enhanced wrinkling was traced back to the fact that C vapor not only permeates
39 through the Gr cover, but also remains within and densifies the Gr. Second, exposure to
40 carbon vapor at ambient temperatures gives rise to the formation of carbon clusters, which
41 form a regular lattice with the periodicity of the moiré of the underlayer graphene with
42 Ir(111). The C clusters are segments of fullerene-type structures bound to the Gr cover. At
43 their baseline substantial rehybridization of the Gr cover to sp^3 , diamond-like carbon takes
44 place. The enormous thermal stability of the C clusters is due to the absence of ripening.
45 They eventually decay by C exchange with the Gr cover which itself feeds the interface with
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3 C atoms that aggregate to Gr underlayer islands.
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5 The exposure of Gr to a C vapor is a strong lever to modify the properties of Gr and to
6 create new Gr hybrid materials. To fully exploit the potential of the interaction of elemental
7 carbon with Gr, in the future it will be important to employ pure vapors of C monomers, C
8 dimers, C trimers, *etc.* This would enable to pin down specific reaction paths, and thus to
9 unambiguously link experiment with modeling resulting in a predictive understanding.
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15 On the negative side, our research indicates that Gr bilayer growth from the C vapor
16 is an unsuitable method for achieving high quality material. For the purpose of bi-layer
17 growth segregation from bulk carbon^{18,40–42} is more suited as it avoids permeation, thus the
18 associated partial C incorporation into the cover layer, and in consequence the enhanced
19 wrinkling.
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25 On the positive side, after removal of the graphene/ C-cluster hybrid from its substrate,
26 *e.g.*, through the H₂-bubbling method,⁴³ we have a new, regularly nanostructured, ultra-thin
27 carbon material at hand. Due to the nanostructured surface, it appears plausible that this
28 material stably binds deposited metal, *e.g.*, Pt, in a finely dispersed way as small clusters. As
29 the material is predominantly sp² hybridized, it should also display good corrosion resistance
30 as an electrode, properties that let our new material appear attractive as a catalyst electrode
31 in fuel cells.^{44–46} Another potential application of our work could be the encapsulation of
32 regular metal cluster arrays on graphene by subsequent carbon vapor exposure and annealing.
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43 Methods

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46 STM and XPS experiments were conducted in ultra high vacuum systems in Cologne and at
47 the I311 beamline⁴⁷ of Max IV Laboratory in Lund, respectively. Prior to each experiment
48 Ir(111) was cleaned by cycles of room temperature noble gas sputtering and flash annealing.
49 Initially, the sample was also treated by O₂ exposure and sputtering at elevated temperature
50 (\approx 1000 K). A fully closed, well-oriented, monolayer Gr sheet was prepared by room tem-
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3 perature ethylene adsorption until saturation, thermal decomposition at 1470 K (Cologne)
4 or 1300 K (Lund), and subsequent high temperature exposure (1270 K in Cologne, 1170 K in
5 Lund) to ethylene.⁴⁸
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9 Carbon vapor was created by sublimation from a C rod, e-beam heated to ≈ 2250 K. The
10 C deposition rate was about 1×10^{17} atoms $\text{m}^{-2}\text{s}^{-1}$ and determined by room temperature
11 deposition, subsequent annealing for Gr formation, and surface area analysis by STM. The
12 integrated C exposure is specified in monolayers (ML), where 1 ML corresponds to $3.8 \times$
13 10^{19} atoms m^{-2} , which is the areal atomic density of a Gr layer. Based on the data of
14 Zavitsanos and Carlson⁴⁹ and at the experimental evaporation temperature, the number of
15 C trimers in the vapor is about twice as high as the one of C monomers, while the number
16 of C dimers is measurably small and all other clusters sizes are marginal.
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19 STM imaging was conducted at room temperature with a typical sample bias U_s ranging
20 from -2 V to +5 V and a tunneling current of $I_t \approx 0.5$ nA.
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23 XP spectra were recorded at room temperature in normal emission. C 1s core levels were
24 measured using a photon energy of 390 eV with a total energy resolution better than 60 meV.
25 Ir 4f core levels were measured with a photon energy of 120 eV and a total energy resolution
26 better than 45 eV.
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29 The first-principles DFT calculations were performed using the plane-wave-basis-set Vi-
30 enna *ab initio* simulation package.^{50,51} The projector augmented wave approach⁵² was used
31 to describe the core electrons and a non-local van der Waals functional⁵³ to describe exchange
32 and correlation. A plane wave kinetic energy cutoff of 400 eV was found to converge energy
33 differences between different configurations within 0.1 eV, which was sufficient for calculating
34 energy differences between different configurations. The same accuracy was achieved with
35 regard to the number of k-points ($3 \times 3 \times 1$) in the two-dimensional Brillouin zone. All struc-
36 tures were relaxed until atomic forces were below 0.002 eV/Å. The calculations were carried
37 out for a 200-atom 10×10 Gr supercell on top of a 9×9 three-atomic-layer-thick Ir(111)
38 slab containing 243 atoms, as in our previous work,^{54,55} or for the same Ir slab without Gr.
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3 20 Å of vacuum was added in the transverse direction to separate the periodic images of the
4 slab.
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8 9 **Supporting Information Available**

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11 The Supporting Information contains as Figure S1 an STM topograph of bilayer Gr on
12 Ir(111), where the undercover Gr island has a slight misorientation with respect to the
13 cover, as Figure S2 a comparison between Gr exposed and not exposed to C vapor at high
14 temperature together with a sketch of the changes due to cool down, and finally as Figure
15 S3 graphical representations for DFT calculations of carbon clusters on Gr/Ir(111) with
16 10, 16, and 58 atoms. This material is available free of charge via the Internet at <http://pubs.acs.org/>.
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26 27 **Acknowledgement**

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29 Financial support of the DFG through project MI581/22-1 *Low energy ion irradiation of*
30 *2D-materials*, of the Bonn-Cologne Graduate School for Physics and Astronomy (C.H.),
31 of the European Commission under a Marie-Sklodowska-Curie fellowship (A. J. M.-G.), of
32 the Swedish Research Council through project 2012-3850 (J. K.), and of the Alexander von
33 Humboldt-Stiftung (C. T.) is gratefully acknowledged. A.V.K. acknowledges Academy of
34 Finland funding through project 286279.
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Graphical TOC Entry

