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Silicon Substitution in Nanotubes and Graphene via Intermittent Vacancies

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Supporting Information

ABSTRACT: The chemical and electrical properties of single-walled carbon nanotubes (SWCNTs) and graphene can be modified by the presence of covalently bound impurities. Although this can be achieved by introducing chemical additives during synthesis, it often hinders growth and leads to limited crystallite size and quality. Here, through the simultaneous formation of vacancies with low-energy argon plasma and the thermal activation of adatom diffusion by laser irradiation, silicon impurities are incorporated into the lattice of both materials. After an exposure of ~ 1 ion/nm², we find Si-substitution densities of 0.15 nm^{-2} in graphene and 0.05 nm^{-2} in nanotubes, as revealed by atomically resolved scanning transmission electron microscopy. In good agreement with predictions of Ar irradiation effects in SWCNTs, we find Si incorporated in both mono- and divacancies, with $\sim 2/3$ being of the first type. Controlled inclusion of impurities in the quasi-1D and -2D carbon lattices may prove useful for applications such as gas sensing, and a similar approach might also be used to substitute other elements with migration barriers lower than that of carbon.



INTRODUCTION

Graphene¹ and single-walled carbon nanotubes² (SWCNTs) are among the most studied materials of the last two decades. Because of the confinement in either one or two dimensions and the fact that they consist exclusively of surface atoms, their properties such as electronic transport and chemical reactivity are highly sensitive to any structural perturbations.^{3,4} Covalent incorporation of foreign atoms within their lattice has thus been proposed as a viable route to engineer their properties.^{5–}

Atomic-scale observations in graphene have shown nitrogen⁸ (N), boron⁸ (B), phosphorus⁹ (P), silicon¹⁰ (Si), and germanium¹¹ (Ge) either as naturally occurring or substitutionally implanted covalent impurities. In SWCNTs, the presence of N,^{12,13} B,¹⁴ P,^{15,16} and Si¹⁵ has been spectroscopically detected in chemically synthesized samples, but no direct transmission electron microscopy (TEM) evidence of their incorporation in the tube walls has been shown. Only for N has such conclusive evidence been presented by Arenal et al.¹⁷ Si impurities have attracted particular recent attention due to the possibility of manipulating them with the focused electron beam.¹⁸⁻²⁰ As a route complementary to chemical synthesis, Dyck et al. recently used a 100 kV scanning TEM (STEM) probe to create vacancies in graphene, which they then managed to fill with Si by irradiating the surrounding amorphous contamination.¹⁹

Motivated further by computational predictions of vacancy formation by argon (Ar) ions by Tolvanen et al.,²¹ we demonstrate here the efficient covalent substitution of Si in both graphene and SWCNTs via an Ar plasma treatment.

RESULTS AND DISCUSSION

Nanotubes were grown in a floating catalyst reactor using ethanol and ferrocene as carbon and catalyst precursors^{22,2} and deposited on commercially available graphene on silicon nitride electron microscopy supports from Ted Pella Inc.^{24,25} The deposition was followed by laser annealing in the Nion UltraSTEM 100 column,²⁶ exposing clean surfaces for later plasma irradiation experiments (Figure 1). An overview of the resulting clean tubes interfacing with graphene is shown in Figure 2a and an atomically resolved closeup in Figure 2b. The images were acquired at 60 keV electron energy and a beam convergence semiangle of 30 mrad. The scattered electrons were detected with a medium angle annular dark field (MAADF) detector at an angular range of 60–200 mrad.

The cleaning was followed by plasma irradiation conducted in a purpose-built plasma target chamber directly connected to the Nion microscope via an UHV transfer system (Figure 1). The argon plasma (pressure 5×10^{-6} mbar) was ignited in a microwave cavity on the side of the chamber and accelerated to a \sim 50 eV kinetic energy, exposing the sample to a dose of \sim 1 ion/nm². Chemical cross-linking and the buildup of amorphous contamination during the experiment was mitigated by concurrently applying ~100 mW of laser power to the sample, which presumably simultaneously helped to

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Figure 1. Experimental system consists of the modified aberrationcorrected Nion UltraSTEM 100 scanning transmission electron microscope in Vienna²⁷ connected to an external plasma chamber via an ultrahigh vacuum (UHV) transfer line. Both laser sources operate at 445 nm wavelength with a power tunable up to 6 W (Lasertack GmbH).²⁶



Figure 2. (a) STEM/MAADF overview of laser-cleaned SWCNTs on graphene. (b) Atomically resolved closeup of the interface. (c) Overview of a plasma-irradiated sample. (d) Closeup showing the presence of impurity atoms after plasma irradiation.

mobilize the Si impurity atoms.¹⁹ This resulted in the preservation of large clean areas, but also patched the contamination in small pockets as for example those visible in Figure 2c. Although not directly observable, these likely correspond to the positions of the greatest lattice disorder and therefore the highest chemical reactivity.

Even within the atomically clean areas and regardless of the laser irradiation, some vacancies especially in graphene remain unoccupied (Figure S1). In our setup, where the mobile carbon and impurity atoms are presumably released by a combination of impacts from the Ar plasma as well as due to thermal activation, this could perhaps in future be prevented by optimizing the laser irradiation parameters to maximize the number of released atoms. We nevertheless find a large number of covalently bound impurity atoms with a scattering contrast similar to Si²⁸ (Figure 2d). To confirm their identity, we used

electron energy loss spectroscopy (EELS) to acquire the elemental fingerprints of each atom.^{9,10} Because our focus was on impurities bound to SWCNTs, we studied the tubes suspended over the holes in the graphene support (Figure 3a).



Figure 3. (a) Overview STEM/MAADF image of SWCNTs in vacuum and incorporating several covalently bound Si atoms. (b) Mapped Si *L*-edge intensity in the 99–200 eV energy window (128 px \times 128 px). (c) Spectrum acquired from the atom highlighted in (a) with spectral features consistent with 4-coordinated Si.¹⁰

The EELS system used here⁹ consists of a Gatan PEELS 666 spectrometer with an energy dispersion of 0.5 eV/px and an Andor iXon 897 electron-multiplying camera. A backgroundsubtracted spectrum recorded from the atom highlighted in Figure 3a is given in Figure 3c, indicating based on the *L*-edge shape and onset at ~99 eV a 4-coordinated Si impurity.^{10,29} The spatial distribution of elements can be likewise analyzed by recording a spectrum from each probe position and by mapping the corresponding core losses. Using the Si *L*-edge intensity (~99–200 eV, see Figure 3c), the Si distribution was mapped and is visible in Figure 3b, confirming the chemical identity of the impurity atoms.

We next turn our attention to the structure and abundance of the Si sites. Two fully saturated substitutions, 3- and 4coordinated configurations (Si-C₃ and Si-C₄, respectively), have been identified in graphene.^{10,29} Our atomic resolution observations, including those in Figure 4, confirm that both



Figure 4. Examples of atomically resolved STEM/MAADF images of (a) Si- C_3 and (b) Si- C_4 impurities in SWCNTs.

configurations are also present in Ar-irradiated SWCNTs. We observed a total of 61 Si sites in 38 tubes (although the configuration could only be identified for 51), with ~63% being Si-C₃ and ~37% Si-C₄. These numbers agree remarkably well with the computationally projected abundance of single and double vacancies formed upon ion irradiation at energies similar to ours.²¹ We likewise observed a large number of Si

defects in graphene (Figure S1), but their relative abundances were not determined.

Interestingly, regardless of the smaller energy required to displace C atoms from SWCNTs,³⁰ this was not reflected in the relative impurity density. We studied a total SWCNT surface area of 1200 nm² that contained the aforementioned 61 Si atoms, corresponding to an areal density of ~0.05 nm⁻². A graphene surface area of 1365 nm² contained more than three times as many Si impurities, 210 atoms in total, with an areal density of ~0.15 nm⁻². While Si impurities are commonly found on graphene^{10,18,29} (although their origin remains unclear), they are not present on SWCNTs such as ours that have not undergone liquid dispersion. It is thus likely that to reach the vacancies created on nanotubes, the Si adatoms are first required to migrate over the graphene surface.

To study the migration energetics, we ran density functional theory (DFT)-based atomistic simulations (details in Methods) with the projector-augmented wave method implemented in the GPAW package³¹ and calculated the binding energies (E_b) and migration barriers (E_m) of Si adatoms on graphene and on a set of achiral SWCNTs (Table 1 and Figure 5). The

Table 1. Calculated Values of Binding Energies (E_b) and Migration Barriers (E_m) for Si Adatoms on Graphene and SWNTs^{*a*}

CNT	site	$E_{\rm b}$, eV	path	$E_{\rm m}$, eV
graphene		0.34		0.06
(7,7)	1	0.82	1-2	0.08
(7,7)	3	0.66	1-3	0.43
(7,7)			3-1	0.27
(15,15)	1	0.46	1-2	0.06
(15,15)	3	0.32	1-3	0.26
(15,15)			3-1	0.12
(12,0)	1	0.95	1-3	0.35
(12,0)	3	0.74	3-1	0.13
(26,0)	1	0.43	1-3	0.19
(26,0)	3	0.33	3-1	0.09
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^{*a*}The corresponding adsorption sites are shown in Figure 5.



Figure 5. Si adsorption sites on (a) (7,7) armchair and (b) (12,0) zigzag SWCNTs reflecting two inequivalent migration paths (1-2 and 1-3).

lowest energy configurations for Si adatoms on both graphene and nanotubes correspond to the bridge site, that is, above a C–C bond. The calculated binding energy on graphene was 0.34 eV, slightly lower than the previously reported values (0.44³² and 0.55 eV³³). This discrepancy appears to arise from differences in exchange–correlation functionals, revPBE versus PBE,³⁴ as with the latter $E_{\rm b} = 0.55$ eV was also reproduced in our calculations. On the surface of nanotubes, the binding energies depend on the tube diameter, chirality, and adsorption site. For smaller diameter tubes, the calculated $E_{\rm b}$ values are significantly higher than those for graphene, while converging to the graphene value as the tube diameter increases. Interestingly, the most reactive C–C bridge never lies on the tubes' axis or along their circumference, but is instead diagonal (sites 1 and 2 in Figure 5). This is different from C adatoms that have been shown to prefer the circumferential bridge configuration on armchair tubes.³⁵

The calculated energy barriers (Table 1) show that migration on armchair SWCNTs prefers the direction of the nanotube axis. For the (7,7) and (15,15) tubes, migration barriers along the path 1-2 are only 0.08 and 0.06 eV, respectively, and are therefore very close to the value in graphene (0.06 eV in our calculations, in excellent agreement with previously reported values of 0.06-0.07 eV).³² By contrast, migration paths around the circumference have barriers 3-5 times higher and are therefore much less likely to occur. Migration on zigzag tubes is less directed. According to climbing-image nudged elastic band (cNEB) calculations for the (12,0) tube, migration along the path 1-2 on the tube circumference always occurs via configuration 3. Meanwhile, the Si adatom jumps between positions that are equivalent to sites 1 and 3 can occur in several directions. The calculated energy barriers for these jumps are higher than those for migration along the axis of armchair nanotubes, and therefore migration of Si adatoms on zigzag tubes will be slower.

It is important to note that the Si migration barriers are much lower than those of C adatoms $(0.47 \text{ eV on graphene}^{36})$ and $\sim 0.6-1.3$ eV on 10-15 Å diameter nanotubes³⁵), which may explain why Si is such a common lattice impurity.^{10,18} Because the barriers in larger diameter tubes are further nearly as low as in graphene, differences in Si migration over the surface of the two materials do not provide a direct explanation for their differing Si concentrations. The fact that we observed many fewer residual vacancies in SWCNTs, however, suggests that C reconstruction in nanotubes is in general more efficient. One possible explanation is that endohedral C adatoms (either endemic or sputtered by the Ar ions) have migration barriers much smaller than those on the outer wall.³⁵ Because these atoms are unable to escape from the quasi-one-dimensional tube, each migrating C will rapidly sample the entire inner surface and recombine with any vacancy it encounters,³ effectively hindering the incorporation of Si by reducing the number of available substitution sites.

Finally, the discussion has so far only concerned Si impurities. We believe, however, that the presented method is more universal and could in principle be used to substitute any element. Several factors will have an impact on the dynamics and efficiency of the process. For example, the filling rate of the vacancies is determined by the availability of the impurity atoms, that is, their concentration and migration rate with respect to C. The migration rate is sensitive to at least the valence electron structure and can vary greatly between different elements. Meanwhile, the vacancy formation and reconstruction rates are largely dominated by the ion energy and the dose rate, but are also affected by the effective temperature. Thus, either guided by computations or a series of trial and error experiments, these process parameters need to be optimized for each case separately, at least if the aim is to achieve a high concentration of perfectly reconstructed impurity sites.

CONCLUSIONS

To summarize, we have used argon ions to create mono- and divacancies in graphene and SWCNTs and demonstrated the

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substitution of Si impurities in both materials with respective concentrations of 0.15 and 0.05 nm^{-2} . The captured Si atoms bonded in both 3- and 4-coordinated configurations were directly identified using atomically resolved STEM and EELS. Finally, our atomistic simulations show that Si migration is substantially faster than that of C. Our findings could enable also other impurities with similar migration barriers to be captured in the graphitic lattice in greater quantities than what has so far been achieved and provide a feasible route for efficient chemical functionalization.

METHODS

Sample Preparation. The SWCNTs were synthesized in a floating catalyst reactor using ethanol (C_2H_5OH) as the primary carbon source and hydrogen (H_2) as a reaction mediator.^{22,23} Ferrocene and thiophene were used in respective roles as a catalyst source and growth promoter. In these experiments, the reactor was fed with 300 cm³ min⁻¹ of H_2 and 300 cm³ min⁻¹ of nitrogen carrying C_2H_5OH at the rate of 4 μ l min⁻¹. The SWCNTs were landed on predeposited monolayer graphene (Graphene Inc.) on silicon nitride membranes acquired from Ted Pella Inc. The deposition times varied between 120–300 s.

The silicon (Si) substitution was achieved by using a custom-made plasma chamber connected to the electron microscope through an UHV transfer system. To create intermittent vacancies in the tube walls, argon ions (Ar⁺) were formed in a microwave plasma cavity at the pressure of ~5 × 10^{-6} mbar and accelerated to a kinetic energy of ~50 eV in the normal direction of graphene. The total radiant exposure in the experiments was ~1 ion nm⁻². To mobilize the Si impurities, the samples were concurrently irradiated with a high-power laser previously used for cleaning 2D materials,²⁶ to allow the filling of the created vacancies. For electron microscope observations, the samples were transferred under high vacuum without exposing them to the ambient atmosphere.

Scanning Transmission Electron Microscopy. Atomicresolution imaging was carried out with an aberrationcorrected Nion UltraSTEM 100 microscope. The instrument was operated at a 60 keV primary beam energy, the vacuum pressure at the sample stage being 2×10^{-10} mbar. The angular range for the MAADF detector of the instrument was 60–200 mrad. The electron energy loss spectra were acquired with an in-house built system consisting of a Gatan PEELS 666 spectrometer operated at an energy dispersion of 0.5 eV/px and an Andor iXon 897 electron-multiplying camera. To record high signal-to-noise ratio point spectra from individual impurities, the probe was parked on the respective atoms for 5-10 s. The spectral images were acquired with a 128 px × 128 px probe array, the dwelling time per pixel being 25 ms.

Density Functional Theory. All simulations were performed using DFT as implemented in the GPAW package.³¹ We used the revPBE³⁸ exchange–correlation functional, a dzp basis set,³⁹ and a grid spacing of 0.2 Å. The length of the models for armchair and zigzag SWCNTs were 12.35 and 12.83 Å, respectively. Graphene was modeled using a 7×7 supercell of 98 atoms. The Brillouin zone was sampled using 8 k-points in the periodic axial direction for nanotubes and a $6 \times 6 \times 1$ k-point grid for graphene. Migration barriers were obtained with the cNEB method.⁴⁰

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b01894.

STEM/MAADF images of silicon-substituted graphene including overview of the lattice with many point defects as well as individual and clustered impurities, an individual silicon atom in four-coordinated configuration, and three nearby silicon impurities PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Geim, A. K.; Novoselov, K. S. The rise of graphene. *Nat. Mater.* **2007**, *6*, 183–191.

(2) Iijima, S.; Ichihashi, T. Single-Shell Carbon Nanotubes of 1-nm Diameter. *Nature* **1993**, 363, 603.

(3) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

(4) Baierle, R. J.; Fagan, S. B.; Mota, R.; da Silva, A. J.; Fazzio, A. Electronic and Structural Properties of Silicon-Doped Carbon Nanotubes. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2001, 64, 085413.

(5) Ewels, C. P.; Glerup, M. Nitrogen Doping in Carbon Nanotubes. J. Nanosci. Nanotechnol. **2005**, *5*, 1345–1363.

(6) Terrones, M.; Filho, A.; Rao, A. Carbon Nanotubes; Topics in Applied Physics; Springer Berlin/Heidelberg, 2008; Vol. 111, pp 531–566.

(7) Ayala, P.; Arenal, R.; Loiseau, A.; Rubio, A.; Pichler, T. The Physical and Chemical Properties of Heteronanotubes. *Rev. Mod. Phys.* **2010**, *82*, 1843–1885.

(8) Bangert, U.; Pierce, W.; Kepaptsoglou, D. M.; Ramasse, Q.; Zan, R.; Gass, M. H.; Van den Berg, J. A.; Boothroyd, C. B.; Amani, J.;

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Hofsäss, H. Ion Implantation of Graphene-Toward IC Compatible Technologies. *Nano Lett.* 2013, 13, 4902–4907.

(9) Susi, T.; Hardcastle, T. P.; Hofsäss, H.; Mittelberger, A.; Pennycook, T. J.; Mangler, C.; Drummond-Brydson, R.; Scott, A. J.; Meyer, J. C.; Kotakoski, J. Single-Atom Spectroscopy of Phosphorus Dopants Implanted into Graphene. 2D Mater. 2017, 4, 021013.

(10) Ramasse, Q. M.; Seabourne, C. R.; Kepaptsoglou, D.-M.; Zan, R.; Bangert, U.; Scott, A. J. Probing the Bonding and Electronic Structure of Single Atom Dopants in Graphene with Electron Energy Loss Spectroscopy. *Nano Lett.* **2013**, *13*, 4989–4995.

(11) Tripathi, M.; Markevich, A.; Böttger, R.; Facsko, S.; Besley, E.; Kotakoski, J.; Susi, T. Implanting Germanium into Graphene. *ACS Nano* **2018**, *12*, 4641–4647.

(12) Keskar, G.; Rao, R.; Luo, J.; Hudson, J.; Chen, J.; Rao, A. M. Growth, Nitrogen Doping and Characterization of Isolated Single-Wall Carbon Nanotubes Using Liquid Precursors. *Chem. Phys. Lett.* **2005**, *412*, 269.

(13) Susi, T.; Kaskela, A.; Zhu, Z.; Ayala, P.; Arenal, R.; Tian, Y.; Laiho, P.; Mali, J.; Nasibulin, A. G.; Jiang, H.; et al. Nitrogen-Doped Single-Walled Carbon Nanotube Thin Films Exhibiting Anomalous Sheet Resistances. *Chem. Mater.* **2011**, *23*, 2201–2208.

(14) Ayala, P.; Reppert, J.; Grobosch, M.; Knupfer, M.; Pichler, T.; Rao, A. M. Evidence for Substitutional Boron in Doped Single-walled Carbon Nanotubes. *Appl. Phys. Lett.* **2010**, *96*, 183110–183113.

(15) Campos-Delgado, J.; Maciel, I. O.; Cullen, D. A.; Smith, D. J.; Jorio, A.; Pimenta, M. A.; Terrones, H.; Terrones, M. Chemical Vapor Deposition Synthesis of N-, P-, and Si-Doped Single-Walled Carbon Nanotubes. *ACS Nano* **2010**, *4*, 1696–1702.

(16) Ruiz-Soria, G.; Susi, T.; Sauer, M.; Yanagi, K.; Pichler, T.; Ayala, P. On the Bonding Environment of Phosphorus in Purified Doped Single-Walled Carbon Nanotubes. *Carbon* **2015**, *81*, 91–95.

(17) Arenal, R.; March, K.; Ewels, C. P.; Rocquefelte, X.; Kociak, M.; Loiseau, A.; Stéphan, O. Atomic Configuration of Nitrogen-Doped Single-Walled Carbon Nanotubes. *Nano Lett.* **2014**, *14*, 5509–5516.

(18) Susi, T.; Kotakoski, J.; Kepaptsoglou, D.; Mangler, C.; Lovejoy, T. C.; Krivanek, O. L.; Zan, R.; Bangert, U.; Ayala, P.; Meyer, J. C.; et al. Silicon–Carbon Bond Inversions Driven by 60-keV Electrons in Graphene. *Phys. Rev. Lett.* **2014**, *113*, 115501.

(19) Dyck, O.; Kim, S.; Kalinin, S. V.; Jesse, S. Placing single Atoms in Graphene with a Scanning Transmission Electron Microscope. *Appl. Phys. Lett.* **2017**, *111*, 113104.

(20) Tripathi, M.; Mittelberger, A.; Pike, N. A.; Mangler, C.; Meyer, J. C.; Verstraete, M. J.; Kotakoski, J.; Susi, T. Electron-Beam Manipulation of Silicon Dopants in Graphene. *Nano Lett.* **2018**, *18*, 5319–5323.

(21) Tolvanen, A.; Kotakoski, J.; Krasheninnikov, A. V.; Nordlund, K. Relative abundance of single and double vacancies in irradiated single-walled carbon nanotubes. *Appl. Phys. Lett.* **2007**, *91*, 173109.

(22) Ding, E.-X.; Jiang, H.; Zhang, Q.; Tian, Y.; Laiho, P.; Hussain, A.; Liao, Y.; Wei, N.; Kauppinen, E. I. Highly Conductive and Transparent Single-Walled Carbon Nanotube Thin Films From Ethanol by Floating Catalyst Chemical Vapor Deposition. *Nanoscale* **2017**, *9*, 17601–17609.

(23) Ding, E.-X.; Zhang, Q.; Wei, N.; Khan, A. T.; Kauppinen, E. I. High-Performance Single-Walled Carbon Nanotube Transparent Conducting Film Fabricated by using Low Feeding Rate of Ethanol Solution. *R. Soc. Open Sci.* **2018**, *5*, 180392.

(24) Laiho, P.; Mustonen, K.; Ohno, Y.; Maruyama, S.; Kauppinen, E. I. Dry and Direct Deposition of Aerosol-Synthesized Single-Walled Carbon Nanotubes by Thermophoresis. *ACS Appl. Mater. Interfaces* **2017**, *9*, 20738–20747.

(25) Mustonen, K.; Hussain, A.; Hofer, C.; Monazam, M. R. A.; Mirzayev, R.; Elibol, K.; Laiho, P.; Mangler, C.; Jiang, H.; Susi, T.; et al. Atomic-Scale Deformations at the Interface of a Mixed-Dimensional van der Waals Heterostructure. *ACS Nano* **2018**, *12*, 8512–8519.

(26) Tripathi, M.; Mittelberger, A.; Mustonen, K.; Mangler, C.; Kotakoski, J.; Meyer, J. C.; Susi, T. Cleaning Graphene: Comparing Heat Treatments in Air and in Vacuum. *Phys. Status Solidi RRL* 2017, 11, 1700124.

(27) Hotz, M. T.; Corbin, G. J.; Dellby, N.; Krivanek, O. L.; Mangier, C.; Meyer, J. C. Ultra-High Vacuum Aberration-Corrected STEM for in-situ studies. *Microsc. Microanal.* **2016**, *22*, 34–35.

(28) Krivanek, O. L.; Chisholm, M. F.; Nicolosi, V.; Pennycook, T. J.; Corbin, G. J.; Dellby, N.; Murfitt, M. F.; Own, C. S.; Szilagyi, Z. S.; Oxley, M. P.; et al. Atom-By-Atom Structural and Chemical Analysis by Annular Dark-Field Electron Microscopy. *Nature* **2010**, *464*, 571.

(29) Zhou, W.; Kapetanakis, M.; Prange, M.; Pantelides, S.; Pennycook, S.; Idrobo, J.-C. Direct Determination of the Chemical Bonding of Individual Impurities in Graphene. *Phys. Rev. Lett.* **2012**, *109*, 206803.

(30) Krasheninnikov, A. V.; Banhart, F.; Li, J. X.; Foster, A. S.; Nieminen, R. M. Stability of Carbon Nanotubes Under Electron Irradiation: Role of Tube Diameter and Chirality. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 125428.

(31) Enkovaara, J.; Rostgaard, C.; Mortensen, J. J.; Chen, J.; Dułak, M.; Ferrighi, L.; Gavnholt, J.; Glinsvad, C.; Haikola, V.; Hansen, H. A.; et al. Electronic Structure Calculations With GPAW: a Real-Space Implementation of the Projector Augmented-Wave Method. *J. Phys.: Condens. Matter* **2010**, *22*, 253202.

(32) Xian, L.; Chou, M. Y. Diffusion of Si and C Atoms on and Between Graphene Layers. J. Phys. D: Appl. Phys. 2012, 45, 455309. (33) Pašti, I. A.; Jovanović, A.; Dobrota, A. S.; Mentus, S. V.; Johansson, B.; Skorodumova, N. V. Atomic Adsorption on Pristine Graphene along the Periodic Table of Elements-From PBE to Non-Local Functionals. Appl. Surf. Sci. 2018, 436, 433-440.

(34) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(35) Krasheninnikov, A. V.; Nordlund, K.; Lehtinen, P.; Foster, A. S.; Ayuela, A.; Nieminen, R. M. Adsorption and Migration of Carbon Adatoms on Carbon Nanotubes: Density-Functional Ab Initio and Tight-Binding Studies. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *69*, 073402.

(36) Lehtinen, P. O.; Foster, A. S.; Ayuela, A.; Krasheninnikov, A.; Nordlund, K.; Nieminen, R. M. Magnetic Properties and Diffusion of Adatoms on a Graphene Sheet. *Phys. Rev. Lett.* **2003**, *91*, 017202.

(37) Gan, Y.; Kotakoski, J.; Krasheninnikov, A. V.; Nordlund, K.; Banhart, F. The diffusion of Carbon Atoms Inside Carbon Nanotubes. *New J. Phys.* **2008**, *10*, 023022.

(38) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved Adsorption Energetics Within Density-Functional Theory Using Revised Perdew-Burke-Ernzerhof Functionals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 7413.

(39) Larsen, A. H.; Vanin, M.; Mortensen, J. J.; Thygesen, K. S.; Jacobsen, K. W. Localized Atomic Basis Set in the Projector Augmented Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *80*, 195112.

(40) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **2000**, *113*, 9901.