Atom-by-atom observations on defect formation and dynamics in 2D materials studied by HRTEM

Dissertation

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1 Introduction

In this work we combine two recent developments each of which opened a huge field of research:

1. High Resolution Transmission Electron Microscopy where recent technical advances in electron optics\textsuperscript{1,2} allow to obtain atomic-resolution images at reduced beam energies. "For their development of aberration-corrected electron microscopy, allowing the observation of individual atoms with picometer precision, thus revolutionizing materials science"\textsuperscript{3} H. Rose, M. Haider and K. Urban received the Wolf Prize in Physics 2011.

2. Two-dimensional materials, the most prominent of which is graphene\textsuperscript{4} first discovered in 2004 by A. Geim and K. Novoselov.\textsuperscript{5} They were awarded for the Nobel Prize in Physics in 2010 "for groundbreaking experiments regarding the two-dimensional material graphene".\textsuperscript{6}

This combination turns out to be extremely fruitful because for the first time it is possible to see single atoms instead of atomic columns in transmission mode. This offers experimental excess to fundamental phenomena in materials sciences that so far have been reserved to computer simulations or analytical theory as capturing the dynamics of individual atoms in a bulk material is beyond the spatial and temporal resolution limit of current characterization techniques. Examples are the atomic structure of amorphous materials or the migration of point defects, grain boundaries and dislocations.

On the other hand, this setup is an excellent lab-bench to study electron-specimen interaction such as the effect of chemical bonding on the elastic scattering,\textsuperscript{A1} changes in the crystal structure due to knock-on (bond rotations\textsuperscript{A3, A5, 7} or sputtering\textsuperscript{A4, 8}) and surface modifications caused by beam induced chemical reactions (chemical etching\textsuperscript{A1, 9, 10}). Furthermore, 2D materials are the thinnest possible membranes and hence attracted a lot of attention as a possible TEM substrate for HRTEM,\textsuperscript{11, 12, 13} electron holography\textsuperscript{14} and as ultra-thin windows for liquid cells.\textsuperscript{15, 16, 17}

In addition, the well defined and simple geometry (especially the precisely defined thickness) and high stability of these new 2D materials allows measurements at a level of accuracy that has not been possible before inspiring researchers all over the world to push the limit of traditional microscopy techniques. Some examples are the detection of chemical bonding in direct HRTEM images for N-doped graphene and boron nitride,\textsuperscript{A1} the possibility to distinguish between different light elements (B, C, N, O) from HRTEM\textsuperscript{A1} and ADF-STEM,\textsuperscript{18, 10} to discern between bottom and top layer in bi-layer graphene from exit wave reconstruction\textsuperscript{19} and the possibility to perform spectroscopic measurements on single atoms.\textsuperscript{20, 21, 22, A10} At the same time all of the above examples have in common that they make quantitative comparisons to simulations and therefore it is necessary to re-evaluate the accuracy and validity of the calculations because they are used at a higher level that they originally were designed for.\textsuperscript{A2}
A very important parameter is the choice of the material that is used for a specific study:

Mechanically exfoliated graphene is an excellent model system with well defined geometry (single crystal without defects, known composition and known thickness) that can easily be prepared in the lab. Hence it offers an excellent starting point to study the response of the material to high-energy electron irradiation. Thereby many parameters can be varied to distinguish different processes (beam energy, beam current, electron dose, temperature, pressure). E.g. the beam energy can be raised to artificially introduce defects into the structure (by removing atoms via knock-on sputtering) and the formation and migration of these defects can be analysed and compared to simulations. For the first times this allowed to directly determine the sputtering cross-section as a function of the beam energy from counting the number of missing atoms as a function of beam energy and electron dose.

Graphene from Chemical Vapour Deposition (CVD) on nickel or copper substrates is technically very interesting because it has excellent quality and the process can be scaled for mass-production to produce graphene for electronic applications such as flexible electrodes for touch-screens. The graphene layers produced by CVD are found to be much more complex because they are polycrystalline where adjacent grains are connected by grain boundaries formed from pentagon-heptagon pairs. We found that electron irradiation it is possible to introduce fluctuations in the grain boundary structure via bond-rotations. By this it is possible to anneal small rotational grains.

N-doped graphene from Chemical Vapour Deposition. By mixing small amounts of ammonium into the CVD process it is possible to introduce substitutional nitrogen into the graphene layer. We were able to detect single atom nitrogen substitutions and for the first time experimentally measured the effect of chemical bonding on HRTEM images for a point defect. Furthermore we found that single atom vacancies in irradiated graphene can be filled by nitrogen atoms what offers an alternative route for the synthesis.
Graphene from Self Assembled Monolayers (SAM) are created from self-organized molecules on gold surfaces that can be cross-linked and removed from the surface. The choice of the precursor molecule and the substrate gives many parameters for tuning the final material. Interestingly, these structures are graphetizing at high temperatures (500-1000 °C) building polycrystalline layers with many point defects and very poor crystal quality. This high defect density makes the material attractive to study chemical etching because this evolves from initial defects (mainly adsorbates) and hence is much more severe in these structures. On the other hand, we found that the crystalline can be increased dramatically (and is comparable to what is obtained by CVD) by performing the same process on a copper surface.\textsuperscript{15}

Structural investigations were also performed for reduced graphene oxide\textsuperscript{11} and graphene from glucose.\textsuperscript{13} Both materials are synthesized by chemical modification of natural graphite and the final graphene structures are between CVD and SAM but they are by far not that homogeneous limiting their use for further microscopy studies.

Single-layer hexagonal boron nitride (\textit{h-BN}) is very similar to mechanical exfoliated graphene because it can also be exfoliated mechanically (also offering very high crystal quality) but the two sub-lattices are occupied by two different atomic species. Under 80kV electron irradiation it shows a very interesting damage formations due to selective sputtering of boron atoms.\textsuperscript{27} Krivanek et al. and Suenaga et al. used the same material to demonstrate that it is possible to distinguish between boron and nitrogen atoms from ADF-intensity and atomic resolution core-level spectroscopy.\textsuperscript{18, 21} Here we used \textit{h-BN} monolayers to demonstrate the effect of chemical bonding on HRTEM images for the first time for a perfect crystal.
Single-layer molybdenum di-sulfide ($MoS_2$) can be mechanically exfoliated from natural $MoS_2$ crystals as well but the structure is very different because the thickness is three layers where the Mo atoms are sandwiched between two sulfurs. Simulations showed that the bottom sulfur atoms are likely to be sputtered at 80kV electron irradiation what we were able to validate experimentally.\textsuperscript{A7} Additionally we found that single-vacancies are getting refilled from atoms on the surface, similar to what we found for nitrogen in graphene. This is an interesting step towards electron beam induced doping of the material.

2D silica glass on graphene was accidentally synthesized in a CVD process. From HRTEM investigations we found that it forms an amorphous 2D network that strikingly resembles Zachariasen's\textsuperscript{28} cartoons of the atomic arrangements in glass from 1932. For the first time these measurements allow to extract radial profile plots and ring statistics from direct images and compare them to different theoretical models. Furthermore we applied a variety of different TEM and STEM imaging and spectroscopic methods as well as DFT simulations to determine the composition of this unknown material. We found that it is a 2D silicon oxide formed from a bilayer of $SiO_4$ tetrahedra that are not covalently bonded to the graphene support. Interestingly, the graphene, besides providing a mechanical support, freeing the silica from the requirement of extreme mechanical stability, plays an important role by energetically stabilizing the 2D silica with respect to bulk $SiO_2$ via van der Waals interactions, as indicated by our DFT simulations.\textsuperscript{A10} Parallel to our investigations Löffler et al.\textsuperscript{29} and Lichtenstein et al.\textsuperscript{30} found the same material in crystalline and vitreous form on Ru and they performed similar analysis based on atomic resolution STM and AFM measurements.

Graphene sandwiching turned out to be an efficient way to minimize electron-beam damage of the enclosed material. Especially 2D heterostructures like single-layer $MoS_2$ sandwiched between two graphene layers offer excellent possibilities to get new insight into the underlying damage mechanisms.
The optics of a transmission electron microscope is in perfect analogy to an optical microscope where instead of photons electrons and are used to create an image. However, instead of glass lenses, electro- and magneto-static lenses are used to control the shape of the probe because electrons, due to their charge, are strongly interacting with all kinds of matter (that’s why the beam can not be shaped by solid objects but only by fields and the beam line needs to be evacuated). While the electrons are penetrating through the sample this extremely strong Coulomb interaction allows to probe extremely small volumes and to obtain very local information. Furthermore the interaction is extremely versatile as besides elastic scattering many different kinds of inelastic electron-electron interactions are taking place that are used for local spectroscopic measurements (EDX, EELS, EFTEM).

In principle all these processes are described by the Dirac equation of all involved particles and fields. All external fields created by the microscope lenses however are slowly varying (mm scale) on the length scale of the electron wavelength (pm scale) and the motion of the electron through the column can be described by particle optics. Within the sample however the propagation needs to be described by quantum mechanics. Hence, high resolution TEM simulation can be separated in three main parts as demonstrated in figure 2.1: First the interaction between the incident electron wave and the specimen is modelled and the specimen exit wave $\Psi_{ex}$ is obtained. Afterwards the specimen exit wave is transferred to the imaging plane by convolve it with the contrast transfer function (CFT) where the characteristics of the microscope and the imaging conditions are included. Finally, the imperfections of the detector need to be taken into account.

## 2.1 Elastic electron-specimen interaction

Because electrons are fermions, the interaction with the specimen is described by the many body Dirac equation of all electrons and nuclei within the sample plus the imaging electrons. In practice a very simple scattering process is assumed where the incident electron is elastically scattered by the combined Coulomb potential of all charges within the sam-
TEM image formation and the influence of chemical bonding

Figure 2.1: Imaging process can be separated in 3 parts: 1) incident electron wave and the specimen, 2) specimen exit wave is transferred to the imaging plane and 3) characteristics of the detector are taken into account.

ple (electrons+nuclei) and all inelastic processes are neglected. This crude approximation simplifies the many body problem to the single-particle problem of the electron propagating in an external potential and the state of the specimen is not affected by the presence of the electron beam. If furthermore the spin and the term proportional to $|eV_s/mc^2| << 1$ is neglected, what is possible for high electron energies,$^{33}$ the propagation of the electron wave is described by a relativistic Schrödinger-like equation (2.1) that can be found in many textbooks.$^{34}$ Thereby, $\Psi(\vec{x})$ is the wave function of the electron at position $\vec{x}$, $m$ is the relativistic mass of the electron and $V_s(\vec{x})$ is the specimen potential.

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 - eV_s(\vec{x}) \right] \Psi(\vec{x}) = E \Psi(\vec{x}) \quad (2.1)$$

For HRTEM simulations, backscattering can be neglected and equation (2.1) can be solved by the multislice algorithm that is explained in more detail in$^{35,34}$ and is implemented in many software packages (e.g. MUSLI$^{36}$, QSTEM$^{37}$). For the study of chemical bonding that was performed for single-layer, light element materials and an acceleration voltage of 80kV it turned out that the linear image approximation (2.3) is justified, as found by comparison of the result with the standard calculation. In this case the specimen exit wave $\psi_{ex}$ is given by equation (2.2) where $V_z$ is the projected specimen potential and $\sigma$ is the interaction parameter.$^{34}$

The final TEM image is obtained by convolving the exit wave with the phase contrast transfer function $F(q_x, q_y) = 2\pi k \left(\frac{1}{2} f \left(\frac{q}{2}\right)^2 + \frac{1}{4} C_s \left(\frac{q}{2}\right)^4 + ...\right)$ that depends on defocus $f$, spherical aberration $C_s$ and higher order aberrations. The exact expression of $F(q_x, q_y)$ can be found in ref.$^{38}$ The convolution can be performed in Fourier space and the image intensity is given by equation (2.4).
2.1 Elastic electron-specimen interaction

\[ \psi_{ex}(x, y) = \exp \left[ i\sigma \int_{-\infty}^{+\infty} V_s(x, y, z) \, dz \right] \psi_{in} = \exp [i\sigma V_z(x, y)] \psi_{in}(x, y) \] (2.2)

\[ \approx (1 - i\sigma V_z(x, y)) \psi_{in}(x, y) \] (2.3)

\[ I_{image}(x, y) = 1 + 2\sigma \text{FT}^{-1} \left[ F(q_x, q_y) \cdot \text{FT} [V_z(x, y)] \right] \] (2.4)

Of course this is a very simple model of the real scattering process that neglects all kinds of inelastic processes by assuming that the state of the specimen is not at all influenced by the presence of the high energy electrons. There are attempts to improve the simulation e.g. by accounting for inelastic scattering via the mutual dynamic object transparency - a concept developed by H. Rose and implemented in computer simulations by H. Müller. Furthermore Chen and Van Dyck showed how to include backscattering and Lee et al. demonstrated that at low voltages, such as 20kV, the linear imaging approximation is not even valid for graphene. Nevertheless, the conventional multislice formalism is still well established and in this work we are using exactly the the same framework (with all its limitations) and instead focus on the question how to obtain the scattering potential.

2.1.1 Isolated atom potentials

For a single, isolated atom, the high-energy electrons are scattered from the Coulomb potential of the nuclei that is screened by the electrons. The combined potential can be calculated by solving the quantum many body problem of all electrons and the nuclei of a single atom. One example are the electron scattering factors published by Doyle and Turner in 1968 that are based on relativistic Hartree-Fock calculations performed by Coulthard in 1967. From this it is possible to calculate the HRTEM contrast of a single atom that mainly depends on the atomic number \( Z \) as can be seen from fig. 2.2.

A TEM sample of cause consists of more than a single atom. Conventionally, the total specimen potential used in the TEM simulation is calculated as a superposition of isolated atom potentials. This model neglects all kinds of inter-atomic interactions within the sample such as the redistributions of electrons due to chemical bonding. It is obvious that this is a very crude approximation and fields that are more sensitive to changes in the electronic state, such as electron energy loss spectroscopy or scanning tunnelling microscopy as well as X-ray diffraction or absorption routinely use much more advanced simulation methods.

2.1.2 DFT potentials

The effect of chemical bonding can be included into the TEM simulation by calculation the total scattering potential by density functional theory (DFT). This approach accounts for the redistribution of electrons within the sample according to their local chemical environment. As we will discuss in the following, this influences the scattering process and alters the absolute and relative contrast observed in the HRTEM experiment.

The use of DFT potentials for HRTEM image simulation was pioneered by Deng and Marks. For bulk oxides, that are known to have strongly ionic bonds, they demonstrated that the effect of chemical bonding should be detectable in the HRTEM micrograph.
2 TEM image formation and the influence of chemical bonding

Figure 2.2: Analysis of atomic contrast for different TEM conditions at 80 kV obtained using a code of E. Kirkland. The red curve corresponds to an uncorrected microscope and the black one to a state of the art Cs corrected microscope as was used in this work. The green curve is obtained when, additional to Cs correction, the focus spread is reduced. This results in better resolution and can be achieved by a monochromator or a Cs corrector. The phase contrast transfer functions for the different microscopes and corresponding values of spherical aberration Cs, defocus f and focus spread df are shown in the inset. Figure adopted from ref. A2

and in practice it is hindered only by the poor specimen quality that can be obtained by traditional ion-beam preparation techniques. The main problems are the amorphous cover layer and the unknown sample thickness. Hence we focused on a completely different class of materials, namely 2D crystals such as graphene and single-layer hexagonal boron nitride, that can be prepared by mechanical exfoliation and by this can overcome the classical limitations.

Our potential simulation is based on Deng and Marks approach with some modifications: First the pseudo-potential DFT code VASP was used for structural relaxation, as we want to study defects such as nitrogen substitution in graphene instead of perfect crystals. This was performed D. Künzal and A. Groß from the department of theoretical chemistry from Ulm University. Second an all-electron DFT calculation was performed on the optimized structure using the WIEN2k software. From this we extracted the 3D electrostatic potential needed for the HRTEM simulation what, in contrast to Deng and Marks, was not done from the X-ray scattering factors provided by the software but directly from the potential files.

In order to produce meaningful results, the new input parameters need to be chosen carefully. Detailed information on the parameters along with example calculations for three model systems (single atom boron and single atom oxygen substitution in graphene and an oxygen ad-atom on graphene) can be found in appendix. A2

In short, we first analysed the potentials provided by the software and found that the initial one (before the calculation started) is basically identical to the isolated atom potentials of E. J. Kirkland that are routinely used for TEM simulations. The charge redistribution due to bonding that is included once the DFT iteration converged acts as a relatively minor perturbation on the initial potential. However, light atoms such as B, C, N and O have
very similar contrast (as can be seen from figure 2.2). Hence already small changes that are not included in comparative simulations can result in misinterpretation of experimental observations.

Due to the divergence of the WIEN2k as well as the Kirkland potentials at the position of the atomic nuclei some technical problems in the discretization are arising. The problem originate from the fact that within the software the potential is available in analytical form but we were only able to access it via a built-in utility software that provides it on a equidistant 3D mesh. We addressed this issue in detail in the references\textsuperscript{35, A1, A2} and found a practicable solution. However, still this is the bottleneck of the simulation as the discretization is very time consuming and, in the future, could tremendously be optimized by getting direct access to the analytical expression of the potential.

Next, we searched for appropriate DFT input parameters for our materials by checking the convergence of the total energy and the electric-field gradient with respect to the number of k-points, the size of the basis set (RKMAX), the Fourier expansion of the charge density (GMAX) and the layer separation. We followed the procedure explained in ref\textsuperscript{53} and used perfect graphene as a test structure. Additionally, we analysed the influence of these parameters on the main quantity we are interested in, i.e., the projected potential and found that it is very robust quantity: The influence of the DFT parameters on the projected potential is smaller than 1.5\% where the absolute difference between DFT and IAM potentials is about 10-30\%. For more information see supporting information of ref.\textsuperscript{A2}

2.1.3 Example calculation

We were able to experimentally validate the advantage of the DFT simulation for two different materials systems:\textsuperscript{A1} First for a perfect crystal of single-layer hexagonal BN where we found that the ionicity of the lattice hinders the distinction between the boron and the nitrogen sub-lattice in HRTEM images at our resolution. Second, for a point defect in graphene - a single-atom nitrogen substitution where one carbon atom was replaced by nitrogen. This nitrogen atom turned out to be detectable in HRTEM micrographs (even though $\Delta Z$ is only one) because it is polarizing the neighbouring carbons\textsuperscript{A1} as we demonstrate in the following.

The starting point for the DFT based HRTEM simulation is the structure model. For the nitrogen substitution in graphene we used a unit cell of $9.87 \times 9.87 \times 20 \AA$ containing one graphene layer (32 atoms) and replaced on carbon by nitrogen. Remarkably, the atomic positions obtained from the pseudo-potential DFT relaxation using VASP are almost identical to pristine graphene. In good agreement with previous reports (e.g.\textsuperscript{54, 55}) C-N and C-C bond length differ by less than 2 pm as can be seen from panel (a) of figure 2.4 (all bond lengths are given in supplementary information of\textsuperscript{A1}). This very much simplifies the separation between bonding effects and structure-relaxation effects (strain) in the final HRTEM images because latter are not present.

This structure model was subsequently used for an all-electron DFT calculation from which the 3D charge- and potential-distribution is obtained. Although these quantities are correlated by the Poisson equation only in three dimensions it turned out to be more intuitive for the interpretation of the calculations on these 2D systems to analyse the
projected charge density and the projected potential. Both of them are shown in figure 2.3 where latter is typically used as input for the multi-slice HRTEM simulation.

Figure 2.3: Analysis of the projected electron charge density (top) and projected electrostatic potential (electrons+nuclei) for a N-substitution in graphene as obtained from the all-electron DFT simulation. (a-d) Analysis of the projected electron density, (a) IAM and (b) DFT result (log greyscale, white corresponds to a higher charge density). (c) Difference DFT-IAM, showing charge rearrangement due to bonding (linear greyscale, white corresponds to a higher charge density in the bonded configuration). Charge differences in the marked regions are given on the right hand side. (d) Charge density difference (DFT-IAM), with periodic components of the graphene removed. The dipole-shaped charge on the carbon atoms next to the nitrogen atoms is indicated in one example as orange-blue line. (e-h) Analysis of the projected potentials, (e) IAM and (f) DFT result (log greyscale). (g) Difference DFT-IAM (linear greyscale). Dark corresponds to high projected potential values. Relative differences listed on the right hand side are (DFT-IAM)/DFT. (h) Difference in projected potentials, with periodic components removed (mask used in d,h is shown as inset). Scale bar is 1 Å.

Figure 2.3 shows the projected electron charge density of all electrons (not only the valance electrons) and the combined projected electrostatic potential of all electrons and nuclei in the system. The first two panels (a) and (b) show the initial projected electron charge density based on an isolated atom model (a) and the DFT result including charge redistributons due to chemical bonding (b). The difference is shown in (c) where the increased charge density between carbon atoms due to $sp_2$ bonding appears white. It is possible to quantify the charge flow due to bond formation by integrating the difference image as we did for special areas. Most interesting, the nitrogen atom that is detectable in the center, remains to be neutral (integration over the red area is almost zero), but results in an reduced number of electrons in the surrounding (integration over green area results in electron deficit of 0.3 electrons). This can be seen much better after removing the strong periodic component of the graphene lattice from the difference image. This was performed with a Fourier filter that is shown as inset in (h). The resulting non-periodic component of the projected charge difference shown in (d) reveals that the nitrogen polarizes the three neighbouring carbons. This results in a net reduction of the number of electrons in the
surrounding of the nitrogen (green area). In the projected potential shown in the lower row (that is the input for the HRTEM simulation) this is reflected in weaker shielding of the core-potentials and consequently stronger scattering of the high-energy imaging electrons within the green area as can be seen in panel (h).

Figure 2.4: TEM simulations for nitrogen-doped graphene. (a) Relaxed atomic configuration for a nitrogen substitution in graphene. Bond lengths are given in angstroms. (b) Projected potential based on the IAM, with the periodic components of the graphene lattice removed, and bandwidth-limited to our experimental resolution (about 1.8 Å). Dark contrast corresponds to higher projected potential values, in accordance with our TEM imaging conditions. (c) TEM simulation based on the IAM potential, for two experimental conditions (Scherzer defocus $f_1 = -9\text{nm}$ and higher defocus with the graphene lattice reflexion in the second extrema of the CFT $f_2 = -18\text{nm}$). Filters are: (i) unfiltered, (ii) periodic components removed by a Fourier filter, and (iii) low-pass filtered. (d) Atomic structure (same bond lengths), with the changes in projected electron density due to bonding shown in colour. Blue corresponds to a lower, red to a higher electron density in the DFT result as compared with the neutral-atom (IAM) case. (e) Projected potential, filtered as in (b), based on the all-electron DFT calculation. (f) TEM simulations using the DFT-based potentials. The greyscale calibration bar applies to columns (ii) and (iii), which are all shown on the same greyscale range for direct comparison. The scale bars are 5 Å.

The effect of this polarization on the HRTEM image formation is shown in figure 2.4 where we compare the neutral atomic configuration in the top row and the bonded configuration (bottom row). From the top row of figure 2.4(c) we find the contrast of neutral N atoms to be less than 0.1% weaker as compared to neutral carbon atoms. This is expected already from figure 2.2 and suggests that it should not be possible to detect nitrogen substitutions in graphene. For the bonded configuration however we find the nitrogen contrast to be
0.3% stronger as for carbon as calculated for Scherzer conditions (marked as $f_1$). However, even the excellent signal to noise level that we can obtain experimentally due to the extremely high stability of the material is not sufficient to detect a difference of only 0.3%. Interestingly, the polarization effect of the nitrogen on the carbons is not a point defect but instead expands over several atomic distances and results in low frequency information. Typically the microscope is operated at Scherzer defocus to create a single transfer band and dark contrast can directly be interpreted in terms of the atomic structure. However, under these conditions the contrast transfer function (CTF) acts as a high-pass filter that removes the low-frequency information on the nitrogen substitution. The transfer of this information can be enhanced by using a larger defocus ($f_2$) (on the expense of oscillations in the CTF and consequently more difficult image interpretation). Now, the nitrogen defect can be detected, yielding a stronger (about 0.6%) and also wider dark contrast for the bonded configuration as evident from the HRTEM simulation shown in the lower row of figure 2.4(c).

![HRTEM images of nitrogen dopants in CVD graphene.](image)

Figure 2.5: HRTEM images of nitrogen dopants in CVD graphene. Imaging conditions and filters in (a)-(f) are the same as applied to the simulated images shown in figure 2.4. The red lines in the CTF plots (insets in (a) and (d)) indicate the 2.13 Å graphene lattice spacing. (a)-(c), Scherzer defocus images. The dark contrast can be directly interpreted as atomic structure. However, the nitrogen substitution defects are not significantly above the noise (red circles). (d)-(f), Larger defocus images ($f_2$) of the same area as shown in the top row. The nitrogen defects are clearly detected as a smooth dark contrast (in any case, a filter ((e) and (f)) is needed to discern the N dopants against the much stronger signal of the single layer graphene lattice). The extended defect (red dashed line in a) allows us to compare the same atomic position in both focus values. (g), Image from a larger area, showing six nitrogen substitution defects marked by red arrows. The inset shows an unfiltered section of the image on the same contrast scale. Scale bars are 1 nm.

In order to validate the findings from the DFT based simulation, we performed HRTEM experiments on nitrogen doped graphene. Therefore nitrogen substitutions where synthesized by mixing small amounts of ammonium into the CVD growth of graphene on copper. Next, we recorded HRTEM image sequences for the two imaging conditions ($f_1$ and $f_2$)
that we used in the simulation. In order to obtain sufficiently good signal to noise ratio for both focus conditions long image sequences (30 frames) were recorded, drift corrected and averaged. As predicted by the DFT simulation, single atom nitrogen substitutions can be detected. Moreover, they exhibit a weak dark contrast in the larger defocus image \( f_2 \) shown in panel (d-g) of figure 2.5 but for Scherzer conditions the contrast disappear below the noise detection limit (2.5(a-c)).

Both, the absolute contrast as well as the focus dependence of the N substitution in the experimental HRTEM images confirm the DFT based simulation result and rule out the prediction of the traditional IAM calculation. This is the first experimental prove that HRTEM images do not contain only structural information (atom positions) but information on the electronic state of the specimen as well. On the one hand, this is important on to avoid misinterpretation of experimental HRTEM data. On the other hand, the charge transfer in point defects such as the nitrogen substitution or nano-scaled crystals such as single-layer \( h \)-BN with lateral sizes of only a few nm (discussed in section 5.1) can not be studied via diffraction experiments.
3 Electron beam induced structural modifications


It was mentioned before that electrons are well suited to probe very small volumes due to their very strong interaction. Besides the elastic scattering, that is most important for HRTEM, many inelastic processes such as electronic excitations (as seen in the EELS and EDX) are taking place. Thereby each process that is changing the state of the sample is called inelastic. Here we are focusing on structural modifications on an atomic scale (not on a scale of single electrons). For graphene it is possible identify two mechanisms that are responsible for the total damage: 1) knock-on damage, that can be understood in terms of simple particle collisions and 2) chemical etching where the specimen is attacked by radicals created by electron irradiation from molecules within the microscope vacuum or the specimen surface. In general there are some more damage mechanisms e.g. local heating and ionization of the specimen (resulting in static electric fields) that are negligible for graphene due to the extremely high thermal and electrical conductance of the material.56,57

The detailed understanding of beam damage is very important because current and future targets of electron microscopy studies face towards gaining quantitative information on an atomic scale where very high electron doses are required (e.g. detection of chemical bonding, single atom spectroscopy and tomography) and towards low-Z, biological materials that have less contrast and are very beam sensitive. It turned out that graphene is extremely stable already at medium beam energies of 80kV that currently are used for structural investigations. This extreme stability offers the possibility to systematically change parameters and, along with the simple structure, makes graphene an excellent lab-system to gain fundamental insight into electron beam induced processes.
3 Electron beam induced structural modifications

3.1 Knock-on damage

Knock-on damage can be thought of as a direct collision of the electron and an atom in the sample where energy and momentum is transferred between the two particles.

Depending on the energy transfer from the $e^-$ to the specimen three scenarios are possible:

1. Sputtering: The energy is high enough to ballistic eject the target atom and a vacancy is staying behind. For very high energies also more complex defect with more than one missing atom can be formed.

2. Bond-rotations: The energy/momentum transfer is not high enough for the target atom to escape the specimen but to result in a bond-rotation. Hence the specimen structure changes but the number of atoms is constant.

3. No structural changes: The excess energy is not high enough to result in sputtering or bond-rotation. Instead it is absorbed by internal degrees of freedom e.g. phonons or elastic deformations.

3.1.1 Sputtering

In the following we will discuss sputtering and bond-rotations in more detail. The probability of atom ejection as a function of the transferred energy is given by the displacement cross-section. In 1929 Mott derived the scattering cross-section of fast electrons by the Coulomb potential of the nucleus. An analytical expression of the Mott scattering cross-section as a function of the ratio between maximum transferred energy $T_{\text{max}}$ and the threshold energy $T_{\text{thr}}$ was published by McKinley and Feshbach in 1948. Thereby $T_{\text{max}}$ depends on the mass-ratio of the two collision partners. Because electrons are very light weight they can only transfer a very small fraction of their total energy to an atom and the energy gets lower for increasing atomic number as nicely demonstrated in [60, Fig2]. The threshold energy $T_{\text{thr}}$, on the other hand, is given by the deformation behaviour (and hence the strength of the chemical bonds and the sputtering geometry) and can be calculated by molecular dynamics or time dependent DFT simulations.

The exact expression of the McKinley Feshbach sputtering cross-section is given by equation 3.1 where $Z$ is the atomic number of the target atom, $E_R = 13.6$ eV the Rydberg energy, $a_0 = 5.3 \times 10^{-11}$ m the Bohr radius of the hydrogen atom, $\beta = \frac{v_e}{c}$ the electron velocity $v_e$ divided by the speed of light $c$, $m_e$ the electron mass and $\alpha \approx \frac{Z}{137}$. $T_{\text{max}}$ as a function of the kinetic electron energy $E = eU$ and the mass of the target atom $m_n$ is given by equation 3.2.

$$
\sigma_D = \frac{4Z^2E_R^2}{m_e^2c^4} \left( \frac{T_{\text{max}}}{T_{\text{thr}}} \right) \pi a_0^2 \left( \frac{1 - \beta^2}{\beta^4} \right) \times \\
\left\{ 1 + 2\pi \alpha \beta \sqrt{\frac{T_{\text{thr}}}{T_{\text{max}}}} - \frac{T_{\text{thr}}}{T_{\text{max}}} \left[ 1 + 2\pi \alpha \beta + (\beta^2 + \pi \alpha \beta) \ln \left( \frac{T_{\text{max}}}{T_{\text{thr}}} \right) \right] \right\} (3.1)
$$

$$
T_{\text{max}} = \frac{2E(E + 2m_e c^2)}{m_n c^2} (3.2)
$$
As can be seen from figure 3.1, the McKinley Feshbach sputtering cross-section is zero up to the threshold energy and rapidly increases afterwards. In 2007, Zobelli et al.\textsuperscript{61} published an electron threshold energy of 113keV for graphene calculated by density-functional tight-binding theory. This finding disagreed with earlier experiments on CNTs where Smith and Luzzi\textsuperscript{62} determined the threshold energy to be below 100keV and gave an exact value of 86keV on the base of MD simulations performed by Crespi et al.\textsuperscript{63} in 1996.

Zobelli et al.\textsuperscript{61} speculate that the 10-20\% overestimation may originate from the curvature or from

"considering the atom sputtering mechanism as a pure knock-on process without any beam-induced electronic excitations. Their effect, as for radiolytic phenomena, is to reduce the bonding energy between the knocked atom and the lattice, in turn, reducing the kinetic energy necessary for atom emission. However, molecular-dynamics simulations based on DFT consider the ground-state electronic wave function and are not able to reproduce any coupling between the dynamical matrix and electronic excitations."

And propose:

"A corrective term could be derived from a precise experimental measurement of the electron energy at which irradiation-induced defects start to appear."
The experiments proposed by Zobelli et al.\textsuperscript{61} have been performed by Meyer et al.\textsuperscript{44} There, we systematically varied the electron energy in the range of 80-100keV and for each voltage recorded time series of initially pristine graphene sheets. From these sequences the sputtering cross-section can be extracted from counting the number of missing atoms as a function of the applied dose. Furthermore the atomic mass was varied by performing the same experiments with "heavy graphene" grown from 99\% $^{13}$C enriched carbon precursors.\textsuperscript{65, 66} As expected, due to the higher atomic mass the $^{13}$C layers are found to be more stable against knock-on damage as compared to $^{12}$C as can be seen in figure 3.2.

Figure 3.2: Damage under 100kV electron irradiation in $^{12}$C (a-c) and $^{13}$C (d-f) graphene. The number of missing atoms as a function of the applied electron dose is given in the inset. The number of displaced atoms vs dose and electron energy for various experiments is shown in (g). The graph in (g) shows the same information for other experiments performed at different accelerating voltages. The slopes of the linear interpolation corresponds to the sputtering-cross section for this specific electron energy and material.

Figure 3.2 shows the experimental derived damage in $^{12}$C (top row) and $^{13}$C graphene (bottom row) under continuous 100kV electron irradiation. As can be seen, for both materials, this energy is sufficient for atom ejection via knock-on sputtering. For $^{13}$C the damage production is much slower what can be attributed to the higher mass but rules out other damage mechanisms such as pyrolysis or chemical etching (discussed in section 3.2) to be responsible for the damage production as these should be identical for $^{12}$C and $^{13}$C. Jannik Meyer repeated this experiment for various other electron energies and the resulting number of missing atoms as a function of the electron dose for each experiment is listed in the graph in figure 3.2(g). This data set allows to calculate the sputtering cross-section for $^{12}$C and $^{13}$C graphene in the voltage range from 80kV-100kV. Further details are found in appendix.\textsuperscript{44}

The experimentally derived sputtering cross-section as a function of the electron energy is shown in 3.3. In good agreement to Smith and Luzzi\textsuperscript{62} the damage is found to start at voltages well below 100kV. However it shows a very smooth onset that can not be explained by the McKinley Feshbach equation (3.1) with a well defined threshold energy. It turned out that Zobellis\textsuperscript{61} proposal that multiple excitations need to be included is not correct. Instead the main contribution to the broadening arises from the assumption that the target atoms are in rest. Interestingly, this was experimentally demonstrated already in 1959 by Brown and Augustyniak.\textsuperscript{67} After including phonons into the McKinley
Feshbach formalism (what was done in the framework of a Debye model) an excellent agreement to the experiments is found. Most interesting, the broadening is not caused by the finite specimen temperature but by the zero-point motion of the atoms (hence cryo microscopy does not serve to avoid knock-on damage) and the model does not have any free parameters. Instead the Debye temperature and $T_d = 109$ keV were taken from literature.\textsuperscript{68, 64} Significant differences between the two models are found only for electron energies smaller than the threshold energy ($U < T_{thr}$) as can be seen from figure 3.3(b). The shaded regions in figure 3.3(a) indicate an uncertainty of a factor of 2 caused by correlative sputtering: Removal of one C atom from graphene creates a single vacancy with 3 under-coordinated carbons that are significantly less stable. One of them is sputtered rapidly and the defect reconstructs into a di-vacancy without dangling bonds. Hence, experimentally we observe the creation of double vacancies rather than the creation of single-vacancies.

![Figure 3.3: (a) Measured and calculated sputtering cross-section for single-layer $^{12}$C and $^{13}$C graphene. The lower boundary of the shaded areas correspond to the calculated cross section, while the upper boundary is twice the calculated value (as would be expected for correlated sputtering). (b) Comparison between the McKinley Feshbach cross-section for a static lattice (grey) and with atom vibrations of the target taken into account (red). For latter, the phonon distribution of the material was approximated in the framework of the Debye model.](image)

In this work we tried to expand the determination of the knock-on cross-section in graphene to higher voltages (100-150 keV). The approach was to irradiate an area of the sample with a specific dose at high energies and afterwards image the material at 80 kV to determine the number of missing atoms because at voltages above 100 keV the damage is too fast to be imaged directly. The analysis of the experiments failed because it needs approximately 1 hour to switch the high tension and setup the microscope. During this time, vacancies can get refilled\textsuperscript{3, 69} from mobile adatoms\textsuperscript{70, 71} and hence the number of missing atoms was always to small. Therefore it was possible to directly image these filling processes. Furthermore, the vacancies are sometimes refilled by non-carbon atoms. Hence high-energy electron irradiation can be used as an alternative route to produce nitrogen doped...
graphene as can be seen in figure 3.4. We observed similar filling processes for beam-induced defects in single-layer $\text{MoS}_2$.\textsuperscript{A7}

![Figure 3.4: Mechanically exfoliated graphene after high energy irradiation (120kV) imaged at 50kV. After the irradiation the initially pristine graphene contains a large number of nitrogen substitutions (arrows). During continuous imaging we observe the formation of two additional substitutions from vacancy sides as indicated by red circles.](image)

In summary, sputtering is well understood, can precisely be modelled for all materials and can be avoided by working at low acceleration voltages. As can be seen later, further simulations and experiments on sputtering for more complex materials such as defects and edges in graphene,\textsuperscript{A3,8} nitrogen doped graphene\textsuperscript{14} or single-layer $\text{MoS}_2$\textsuperscript{A7} were performed.

Before we want to focus on another possible reaction of the system to the impact of high energy electrons - namely bond-rotations.

### 3.1.2 Bond-rotations

Another type of knock-on damage are bond-rotations. The process is exactly the same as for sputtering except the transferred energy is to small for the target atom to escape. Nevertheless this can cause structural modifications of the material the simplest of which is the creation of a Stone-Wales (SW) defect in initially pristine graphene.\textsuperscript{A3,72,73} We performed extensive DFT based tight binding simulations on the formation of the Stone-Wales defect in different sputtering geometries\textsuperscript{A3} and found that typically a transferred energy of $T_{\text{max}} - 1$ eV (for some special geometries even $T_{\text{max}} - 2$ eV) is sufficient to create a SW defect what in terms of electron energies is about 5.4 keV (10.8keV) below the static knock-on threshold. Furthermore we were able to identify two different processes involving either a “circling” or a “nudging” motion as described in detail in appendix.\textsuperscript{A3} So far the simulations do not include lattice vibrations but we assume that they should have a similar broadening effect as found for atomic ejections (especially same magnitude). Experimentally we found that bond rotations are still possible at electron energies of 50keV as can be seen from figure 3.5.

Similar to knock-on sputtering, bond-rotations can be understood in terms of simple particle collisions and (in the static lattice approximation) the involved energies, transformation
Figure 3.5: Modification of defects in graphene under 50keV electron irradiation. Panel a) and b) show the same defect that changed under electron irradiation. The precise atomic configuration can not be obtained because at these low voltages the microscope resolution is not sufficient to obtain lattice resolution. Nevertheless structural changes can be observed indicating that e-beam induced bond-rotations are present. The defects were created by brief irradiation with 300keV electrons of a mechanical exfoliated graphene layer similar to what was used by Kotakoski et al.73

routes in various geometries can precisely be modelled by molecular dynamics simulations. The energy barrier for a bond rotation is about 5eV74,75 what can easily be overcome by electron irradiation but makes thermal activation at room temperature basically impossible.76 A cross-section for bond-rotations has not been published however and, in order to obtain a precise picture on the range of electron energies for which these transformations are possible, it is necessary to include the effect of lattice vibrations - similar to the thermal broadening of the sputtering cross-section discussed in section 3.1.1.

3.2 Chemical etching

The process of electron-beam induced deposition50 (EBID) or removal77 of hydrocarbons is well known.78 The deposition of carbon films on surfaces from organic vapor under electron- and ion-irradiation has been reported by Steward79 already in 1933 and nowadays is used in 3D-EBID lithography for template free fabrication of nano-structures e.g. to write electrical contacts or to repair photo masks. Relative little attention however was paid to these processes in the field of TEM as traditionally the specimen surface is of minor interest. The deposition is usually a practical problem that one tries to minimize by plasma cleaning of the samples. For graphene in contrast, we observe the nucleation and growth of extended holes. This process is called chemical etching and can be used for direct patterning of carbon materials in e-beam lithography processes at electron energies well below 10keV.77 The first systematic study on the chemical damage on carbon nanotubes inside the TEM was performed by Mølhave et al.9 They performed experiments at different vacuum levels (with and without cold trap) and found that

"water vapour, which is present as a background gas in many vacuum cham-
Electron beam induced structural modifications can damage the nanotube structure through electron beam-induced chemical reactions such as:

\[
\begin{align*}
C + 2H_2O &\rightarrow CO_2 + 2H_2 \\
C + O_2 &\rightarrow CO_2 \\
C + \frac{1}{2}H_2 &\rightarrow CH
\end{align*}
\]

In this work we compared the hole growth in graphene at different voltages (20keV and 80keV) by measuring the hole perimeter as a function of the applied dose as shown in Figure 3.2. Most important, we find that chemical etching is basically independent of the electron energy. At low energies it might even be slightly more severe because at 80kV the hole growth is additionally supported by knock-on damage via sputtering of edge atoms. Second, in spite of similar irradiation conditions, strong variations between different experiments are observed. Most likely this is caused by different vacuum conditions due to different sample holders and pumping times. In general the growth slowed down after extended pumping and the use of a cold trap. The inverse behaviour was found for very bad vacuum conditions, e.g. leaking holder or de-freezing of the cold trap, where the damage was too fast for direct imaging.

Figure 3.6: Analysis of chemical etching on graphene at different voltages. a)-c) typical time series of double-layer graphene imaged at 20kV and of mono-layer graphene at 80kV d)-f). The damage was quantified by measuring the hole perimeter (indicated by the dashed lines) as a function of the applied dose. g) shows the result from various experiments performed at 20kV (red) and 80kV (black). Solid and dashed lines denote separate experiments with presumably different (although uncontrolled) environmental conditions.

In addition we observe a strong correlation between the nucleation of holes and contaminations sites as can be seen from figure 3.7 panel a) and b). This indicates that the contaminants contain atomic species that catalyse the chemical destruction of graphene. Further evidence for this is found in the image sequence shown in panels c)-k) of figure 3.7.
where a hole originates from a single foreign atom and a double vacancy. In this experiment, graphene was irradiated at 80keV at a very high electron dose rate \((\approx 8 \times 10^7 \, \text{e}/\text{nm}^2\text{s})\):

For a very long time nothing happens except the formation of some double vacancies one of which is visible in the lower right of panel c). Then a carbon atom is replaced by another atomic species. Most likely this is a metal atom but it is not possible to identify the atomic number from the HRTEM image contrast and it was not deposited artificially. Si and Fe impurities in single- and double-vacancy configurations were reported by Ramasse et al.\(^{80}\) and Chisholm et al.\(^ {22}\) Other candidates are Au and Cr as they are typical contaminants of the Quantifoil films used here. Afterwards again nothing is happening for a longer time except an additional carbon atom next to the metal is removed and the double vacancy undergoes several bond-rotations and diffuses towards the metal. Once the double vacancy meets the metal it seems like the metal has more space and a rapidly growing hole is formed.

![Figure 3.7: Effect of contaminants on the chemical destruction of graphene under 80kV electron irradiation.](image)

**Figure 3.7:** Effect of contaminants on the chemical destruction of graphene under 80kV electron irradiation. a) shows the initial state of the sample and b) after a dose of \(10^9 \, \text{e}/\text{nm}^2\). As can be seen that the growth of extended holes in graphene is always induced by contamination. c)-k) shows an image sequence recorded at a very high dose rate of \(7 \times 10^7 \, \text{e}/\text{nm}^2\text{s}\). c) lattice is still intact (after a dose of \(4 \times 10^{10} \, \text{e}/\text{nm}^2\)) except a double vacancy that formed due to sputtering. d) a carbon atom is substituted by metal. f) another carbon next to the metal is removed and the di-vacancy is migrating towards the metal via bond rotations. h)-i) once the vacancy meets the metal it has more space and the graphene edges are attacked by chemical etching resulting in rapid hole formation. The dose per frame was approximately \(7 \times 10^7 \, \text{e}/\text{nm}^2\) and frame numbers are indicated.
These experiments indicate that the chemical etching does not only depend on the vacuum values (e.g. partial pressure of water). Instead the presence of catalytic atoms seems to be very important especially in the initiation the damage. This may be similar to the influence of catalytic metal ad-atoms aiding in the dissociation of precursors such as ethylene or acetylene in the graphene synthesis as studied from first principles calculations by Gong et al.\textsuperscript{81} Experimentally these processes can be studied in much more detail by artificially combining carbon materials with special metals and study the reactions in-situ. One interesting lab system are single walled carbon nanotubes filled with metals. Chamberlain et al.\textsuperscript{82} demonstrated how a rhenium atom inside a carbon nanotube can bind to the side wall via creation of a $\text{ReC}_2$ molecule resulting in a weak point susceptible to e-beam damage. Utilizing the same approach, Zoberbier et al.\textsuperscript{83} studied the behaviour of various metals clusters (W, Re, Os) with the nanotube and found that the reactivity is determined by the metal to nanotube bonding energy and the amount of electronic density transferred between metal and SWNT.

In order to avoid this chemical destruction not only it is necessary to improve the vacuum system but also the specimen support grids need to be chosen very carefully. Furthermore specimen storage, cleaning and transferring techniques need to be optimized in order to make the samples suitable for UHV investigations. This expertise most likely is available in the field of surface physics (e.g. scanning tunnelling microscopy) and needs to be transferred. In section 6.2 we will demonstrate an alternative route, namely graphene sandwiching, where the specimen is encapsulated between two graphene layers that are offering a precisely controlled chemical environment instead of an undefined high-vacuum atmosphere.

For graphene, however, chemical etching is not hindering the TEM investigations. Instead it is simply limiting the applicable dose on the sample and hence the measurement time. In the case of graphene, the sample is stable enough to allow atomic resolution TEM imaging for about one hour (at typical dose rates of $1 \times 10^6 \text{e}/\text{nm}^2/\text{s}$) after which a sample area with a diameter of roughly 100 nm is destroyed.

Additionally, from experiments on self-assembled monolayers (SAM) imaged with the heating holder, we have indications that chemical etching can strongly be reduced by working at elevated specimen temperatures. Similar to graphene, the SAM samples are extremely thin carbon membranes that are produced from cross-linked, self-assembled molecules on gold surfaces.\textsuperscript{84, 85} By heating to very high temperatures ($>900^\circ\text{C}$), these cross-linked sheets can be converted to nanocrystalline graphene\textsuperscript{86} and atomic resolution imaging has been demonstrated. However, for the cross-linked but non-pyrolized SAMs we found that atomic resolution imaging at room temperature is hindered by extremely strong beam damage. This is what we would expect from our experiences because already in graphene open edges are strongly attacked by chemical etching and the cross-linked samples are expected to form very porous structures. Interestingly we found that at elevated specimen temperatures (400$^\circ\text{C}$), the damage is dramatically reduced as can be seen from the dark field images in figure 3.8 where the sample was irradiated with the same dose at two different temperatures. At room temperature the material was completely removed while at 400$^\circ\text{C}$ the sheet seems to be almost undisturbed.
3.2 Chemical etching

Figure 3.8: Temperature dependence of chemical etching in cross-linked SAM. The four positions indicated by arrows were irradiated with 80kV electrons at a dose of approximately $5 \times 10^8 \text{e nm}^{-2}$. As can be seen from the dark-field images the damage is dramatically reduced at higher temperatures: At room temperature a hole was burned into the carbon film while at 400°C the film is almost undisturbed.

The strong temperature dependence can arise from two factors: First, higher mobility of carbon ad-atoms and hence higher self-repair rate or second (and in my opinion much more likely) the evaporation of water from the specimen surface. More systematic experiments would be necessary to clarify this.

One major problem, when working at higher temperatures is the mechanical stability. With a special in-situ Joule heating setup, we demonstrated that atomic resolution imaging of graphene up to temperatures of 2000K is possible. However in general, this is extremely difficult already at slightly elevated temperatures (some hundred K) due to thermal drift of the sample carrier. Even more important, for many samples, especially thinking about biological applications, this approach is not feasible as they degenerate at high temperatures.
4 Electron beam engineering


O. Lehtinen, S. Kurasch, A. V. Krasheninnikov, and U. Kaiser, “Birth, motion, interaction, and annihilation of dislocations in graphene at the atomic scale”, submitted

In the previous chapter we demonstrated the use of graphene (and other carbon materials) as a model system to gain detailed insight into electron beam-damage in these materials. From this we can drawn two important consequences:

1. Damage free imaging: The acquisition parameters (especially the primary beam energy) can be adjusted to avoid damage. This allows to study the pristine state of the material targeting questions related to the synthesis.

2. Electron beam engineering: Beam damage can explicitly be used to introduce changes in the material (nano-structuring, defect engineering or phase transformations such as amorphization).

Latter makes the TEM a very versatile tool to very locally introduce structural changes and at the same time directly observe their evolution in real time and on atomic scale.

Already for perfect graphene, the combination of chemical etching, bond rotations and sputtering can result in very unexpected transformations such as the formation of other low-dimensional carbon allotropes as shown in figure 4.1. Thereby fullerenes and CNTs are well known and can also by synthesized by chemical routes. Single atom carbon chains however have not been reported before and, so far, high energy electron irradiation of single-layer graphene\textsuperscript{87,88,89} or CNTs\textsuperscript{90} is a unique tool for their production. The transport properties of atomic-sized conductors that can be built from carbon,\textsuperscript{91} gold\textsuperscript{92} or molecules\textsuperscript{93} are of great scientific interest.\textsuperscript{94} Remarkably, the idea for fabricating artificial carbon structures by design (nanoribbons/CNTs) via cutting of defined shapes into multilayer graphene and subsequent high temperature annealing has been proposed already by Ebbesen and Hiura\textsuperscript{95} in 1995.
Figure 4.1: top: (a) Graphene, the mother of all graphitic forms [4, Fig. 1], and (b) a route for the creation of artificial carbon nanostructures from graphite via mechanical shaping with an AFM tip followed by high-temperature annealing proposed by Ebbesen et al. [95, Fig. 6]. middle: Transformation of single-crystal graphene to other low-dimensional carbon compounds initiated and imaged by high-energy electron irradiation: (c) fullerene created under 80kV electron irradiation at room temperature [96, Fig. 1,2]. (d+e) synthesis of a single-walled CNT and a graphene nano-ribbon by high-temperature (∼700°C), high-energy (300kV) electron-beam sculpting of single- and few-layer graphene demonstrated by Song et al. [89, Fig. 3]. bottom: Creation of single-atom carbon chains by electron beam thinning of a carbon fibre [97, Fig. 1](f), CNT [90, Fig. 1](g) and single layer graphene [87, Fig. 1](h).
In TEM mode, carbon chains are frequently observed. We additionally tried to create and image them in STEM mode. These experiments were performed at a probe-corrected Nion UltraSTEM at Cornell University. We continuously scanning the 60kV electron probe over the single-layer graphene specimen and waited for the steadily growing holes to merge and form single atom carbon chains but we were not able to detect them. Most likely they did form but the direct imaging was hindered by the high mobility of the chain along with the sequential image acquisition and the (laterally) strongly inhomogeneous illumination (the highly focused electron probe produces an electrostatic potential with very strong gradients). Hence we think that the chains were not stable during the acquisition but instead were shifted away by the electron probe. But interestingly, it was possible to observe the fullerene formation in STEM as shown in figure 4.2, that before was reported only in TEM mode.

![Figure 4.2: Creation of fullerene from graphene recorded in STEM mode at Nion UltraSTEM operated at 60kV. a) bright field and b) corresponding HAADF dark field image.](image)

In the following we will concentrate on the modification of existing defects in graphene that either are introduced during the growth, such as grain boundaries, or by atom removal of initially pristine structures.

### 4.1 Transformation of double vacancies

In section 3.1.2 we discussed that the impact of high-energy electrons can result in bond-rotations what, in the simple case of perfect graphene, results in the formation of a Stone-Wales defect. Here we demonstrate that by exactly the same mechanism, di-vacancies can transform between three different types all of which have very similar formation energies as predicted earlier. Moreover, multiple transformation can result in lateral migration of the defects as can be seen from figure 4.3 where a di-vacancy initially is observed in the $V_2(555\text{-}6\text{-}\overline{7}\overline{7})$ configuration, then, under continuous 80kV electron irradiation, undergoes two transformations to $V_2(555\text{-}\overline{7}\overline{7})$ and $V_2(5\text{-}8\text{-}5)$. Finally the di-vacancy again has the initial configuration but is migrated by one lattice plane. In this study, the initial defect was created by brief irradiation with 150kV electrons of pristine graphene but the transformation is stimulated and imaged by 80kV electrons.
Figure 4.3: Experimental images illustrating SW transformations in the atomic structure of di-vacancies and migration of these defects. Panels (a)-(d) show sequential HRTEM images of the same defect (in the lower row with structure overlay). (a) $V_2(5555-6-7777)$ transforming into $V_2(555-7777)$ (b) and $V_2(5-8-5)$ (c). Each of these transitions can be explained by a single bond rotation. In the later frame (d), the defect is again a $V_2(5555-6-7777)$, but shifted by one lattice parameter. Scale bar is 1 nm. Figure adopted from [A3, FIG. 6]

In the energy range used here, sputtering exclusively results in formation of isolated double vacancies (creation of single vacancy and sputtering of one of the three under-coordinated carbons). More complex defects with more than two missing atoms are not created from a single sputtering event. The migration of di-vacancies via multiple bond rotations becomes especially interesting for increasing defect densities as it provides a route to vacancy interaction. To explore this, Kotakoski et al. performed experiments at 100kV where atoms are continuously ejected but the damage is still slow enough to be directly imaged and at the same time transformation and migration via bond-rotations are possible. They find, that isolated di-vacancies are clustering and form either extended line defects or more complicated defect structures built from a 30° rotated kernel of hexagons that is surrounded by a chain of alternating pentagons and heptagons. Additionally they were able to show via DFT simulations, that these defects are energetically favourable above isolated di-vacancies and that the ”kernel” defects are semiconducting. As we discuss later in section 4.3 and appendix A6 defects in graphene do interact via out-of-plane corrugations of the membrane what was not taken into account here.

Figure 4.4: Formation of rotated-hexagon kernels in multivacancy structures under a 100 keV electron beam. Adopted from [73, FIG. 3.5] with permission of the authors. Scale bar is 1nm.
Under further irradiation, Kotakoski et al.\textsuperscript{73} created more and more complicated defect structures until the initial crystalline order was completely lost as shown in figure 4.5. They transformed the single crystalline hexagonal graphene sheet into a two dimensional amorphous membrane composed of $sp^2$ hybridized carbon atoms.

This study nicely demonstrates that beam damage in graphene is very versatile but still many results can be interpreted in simple terms of particle collisions via sputtering and bond-rotations. Nevertheless, the final result can be very counter intuitive as (at least my) initial guess would have been that the graphene transforms into a highly perforated crystalline membrane when more and more atoms are removed. Furthermore, they showed that the defect structures are semiconducting. This opens the way to utilize a high energy electron beam for local engineering of the electrical properties of graphene as proposed already in 2009 by Warner et. al.\textsuperscript{99} Later, the same group also demonstrated the spatial control of the defect formation.\textsuperscript{100} Further theoretical work on the systematic amorphization of crystalline graphene sheets via bond-switching has been performed by Kumar et al.\textsuperscript{101}

### 4.2 Grain boundary migration

To date, a huge variety of graphene synthesis methods emerged. One of the most important ones is chemical vapour deposition (CVD) where, at high temperatures, graphene is directly grown on catalytic transition metal surfaces from carbonaceous vapor. In contrast to mechanical exfoliation, these samples are polycrystalline. Interestingly the growth can be optimized to produce predominantly single layers and grain sizes up to millimetres are achievable on copper and platinum.\textsuperscript{102,103,104}
We worked on CVD graphene grown on copper foils that were synthesized by V. Skákalova and J. Smet from MPI Stuttgart. Sometimes the samples were clean enough to allow for atomic resolution imaging also of the grain boundaries (GB). As predicted by theory, we find the GBs to be built from chains of pentagon-heptagon pairs and the orientation and separation of these dislocation cores depend on the grain angle as can be seen from figure 4.6. For special angles highly symmetric, straight GBs with very low energies can be formed. Experimentally, the grains are randomly oriented and the GBs are no longer straight but instead take on meandering, locally curved configurations to reduce lattice strain. This can result also in out-of-plane buckling of the membrane.

Better insight into the structure of polycrystalline graphene samples can be gained from combining dark-field and high-resolution TEM. An overview of our sample can be found in figure 1 of ref. The most interesting quantities, regarding the optimization of the synthesis, are the distributions of grain size and the relative rotation angle as derived earlier from DF-TEM, selected area electron diffraction and AFM. In contrast to the earlier works, our grains were smaller by about one order of magnitude and hence we had to extract the statistics on relative rotation angles directly from atomic resolution images. Even though graphene is known to grow non-epitaxial on copper, we find a strong propensity for neighbouring grains to be misoriented by $\theta \approx 30^\circ$. This is because the statistics is dominated by small grains (with lateral size below 10nm) for which this is the lowest energy crystallographic configuration. This is true of course also for bigger grains but it is clear that if two infinite grains meet at a random tilt non of them will rotate to make a $30^\circ$ boundary although this would be energetically favourable. It seems like there is a critical diameter below which this transition is possible and small grains can...
rotate to accomplish energetically favourable configurations - the most extreme of which is definitely $0^\circ$ (pristine structure).

In the following we want to focus on the question what happens to the more complex defect structure of the grain boundaries under electron irradiation. Is it possible to induce migrations due to bond rotations? Therefore we carried out special experiments where we searched for clean GBs and imaged them over a very long time. We find that it is possible to induce structural fluctuations as can be seen from figure 4.7. For straight GBs however, the bond rotations do not have a preferential direction and hence the boundary is not migrating but instead fluctuates between different shapes around a more or less straight configuration.

![Figure 4.7: Bond-rotation mediated configurational changes of a GB with low curvature.](image)

The image sequence shows the same GB during prolonged electron beam exposure (total time: 12min, dose rate: $2 \times 10^7 e/nm^2/s$, high tension: 80kV). The rotation of the complete lattice at the end of the sequence is caused by chemical etching of holes outside the field of view.

To get deeper insight into this complicated material system, Monte Carlo and DFT based simulations were performed by O. Lethinen, J. Kotakoski and A. Krashenninikov from Helsinki University. First they found, that the GB energy per unit length ($\gamma$) is basically identical for straight and serpentine like boundaries. Interestingly this means that the total energy depends only on the length of the GB but not on the detailed atomic configuration. Hence, the system can minimize the energy by minimizing the length of the grain boundary and the driving force (per unit GB length), $\gamma/R$. For straight boundaries ($R \to \infty$) there is no preferred direction of migration, but small grains ($R \to 0$) should shrink.
Taking this to its logical conclusion, we expect to observe shrinkage of small grains to the point of complete disappearance. This results in the restoration of the perfect structure if no missing atoms are involved in the process or the emission of a vacancy when the initial GB contains a density deficit. Both of these processes are indeed possible and can be induced and directly observed via high-energy electron irradiation in the TEM as be seen from figure 4.8.

Figure 4.8: (a) HRTEM image sequence showing the disappearance of a flower defect under an electron flux of approximately $1.0 \times 10^7 e/(nm^2 s)$ during a 30 s total exposure. (b) energy landscape of this transformation. The two initial bond-rotations increase the total energy by about 3eV. This high energy barrier renders thermal activation of the process basically impossible. (c) shrinking of small grain and its transformation into a flower defect (lower left) and shrinkage of a grain with non-zero density deficit by emission of a di-vacancy.

Interesting, the flower defect seen in panel (a) of figure 4.8 has been reported earlier in both nitrogen-doped$^{113, A1}$ and pristine graphene$^{114, 115, 116}$ and is the most prevalent grain structure in our CVD graphene samples. From further calculations we found that the system can gain an energy of about 7eV from annealing the flower defect. Before it needs to overcome an energy barrier of $\sim 3eV$ in form of two consecutive, energy increasing bond-rotations in the initial stage of the transformations (see panel b of figure 4.8). This high barrier is very unlikely to overcome thermally$^{76}$ and hence electron irradiation may be a unique tool for the annealing of this defect. For more details see appendix.$^{A5}$ In addition, this study gives us an important hint for the frequent observation of this, energetically unfavourable defect: It may be formed from shrinkage and rotation of small grains during the high temperature synthesis (in favour of the bigger grains). By this, either they end up at the flower defect as the barrier for further shrinkage can not be overcome or with the pristine lattice when the rotation, by chance, occurred to happen in the other direction.

At the moment, these are speculations but we showed that by combining HR-TEM and 2D materials allows to get experimental insight into the mechanism of grain boundary migration on atomic scale what so far has been reserved for computer simulations or analytical theory.
In this context our present work can be seen as proof of principle experiments offering plenty of room for further research regarding more specialized questions like: i) the migration of triple points where 3 GBs meet or ii) what happens to straight GBs under electron irradiation when we add an external stimuli to break the symmetry of the two grains. Latter could be mechanical strain, an electric current of a heat gradient across the GB that could be applied in-situ and the reaction of the system could be followed on atomic scale. iii) do the structural fluctuations observed in straight GBs shown in figure 4.7 follow a Maxwell-Bolzmann distribution? By this it would be possible to assign the electron dose rate to a "temperature".

4.3 Graphene at high electron dose rates - Creation, migration and annealing of dislocations

Kotakoski et al.\textsuperscript{73} showed that initially pristine graphene can be amorphasized by 100kV electron irradiation. As, at 80kV, the sputtering cross-section (discussed in 3.1.1) is very small but still non-zero and the chemical etching does not depend on the dose rate, we checked if amorphous graphene can also be produced at this lower voltage by using much higher dose rates. This would offer the possibility to perform EELS experiments on highly defective graphene without the need to switch the high tension. In practice we observe a different reaction of the system. The initial assumptions were correct: Atoms can be removed and etching is not an obstacle. But lowering the voltage strongly influences the ratio between number of sputtered atoms and the number of induced bond rotations. Assuming that latter is constant, we have about 4 orders of magnitude more bond rotations per atom removal at 80kV as compared to 100kV ($\sigma_{Gr}(80kV) = 6 \times 10^{-5}$ barn and $\sigma_{Gr}(100kV) = 0.7$ barn according to the theoretical sputtering cross-section including lattice vibrations discussed in 3.1.1. Note that this comparison is not very accurate because at low voltages the curve rapidly goes to zero and in this regime the absolute values are very sensitive to the threshold energy.).

Instead of creating a highly defective unordered sheet, we observe that the defects are rearranged to lines and produce two isolated dislocations with one row of missing atoms in between. During continuous irradiation and continuous atom removal, these dislocation dipoles further separate (migration along the climb plane) and interact with neighbouring dislocations via out-of-plane distortions as explained in detail in appendix.\textsuperscript{A6} Finally two dislocations can annihilate locally resulting in the restoration of the pristine lattice with one missing row of atoms.
The migration and interaction of dislocations is of key interest in materials science as it largely defines the mechanical properties (especially plastic deformations) and can be studied here with single-atom accuracy. Similar studies have been performed before Warner et al.\textsuperscript{7} However they misinterpreted the out-of-plane corrugations as in-plane strain.

Of course, in these experiments also a big number of double vacancies is observed. Interestingly, in this complicated combination of atom removal, point defects and dislocations, we observed the creation of a flower defect.

Figure 4.9: Creation, migration and annihilation of dislocations in graphene formed under very intense 80kV electron irradiation (dose rate: $7 \times 10^7 e/nm^2/s$). For better visibility strong Gaussian and maximum filters were applied. More details and unfiltered images can be found in appendix.\textsuperscript{A6}

Figure 4.10: Creation (a-e) and annihilation (f) of a flower defect.
From personal communication on a poster,\textsuperscript{117} we heard already from Alex W. Robertson (University of Oxford, Materials Department), that they created the flower under similar conditions. In the mean time this work is published.\textsuperscript{100} Unfortunately we did not get any information on the actual process that finally resulted in the flower. However it is difficult to imagine that it follows the same route as the annihilation of the flower discussed in section 4.2 as this would imply 4 energy increasing bond-rotations with a total energy of 10eV. Here we find that the route for the creation is completely different because dislocations are involved in the progress. This results in a local increase of the number of carbon atoms as can be seen from figure 4.10. Such additional factors can tremendously change the energetics of the process as we demonstrated for the annealing of the flower in the presence of a di-vacancy and an ad-atom pair (see figure 4c of ref\textsuperscript{A5}).
Soon after the discovery of graphene and its extraordinary properties, researchers started to explore the use of mechanical exfoliation for the preparation of other 2D materials from natural bulk crystals. Of course the main focus was on materials with very similar structures (weakly interacting layers that can be separated e.g. by mechanical cleavage) but very different electrical properties.\textsuperscript{49,118} Remarkably, this idea is not at all new as electron diffraction on exfoliated thin sheets of MoS\textsubscript{2} (thickness $\ll 40\text{ Å}$) have been performed already in 1936 by Finch and Wilman.\textsuperscript{119} In the late 60th Frindt et al.\textsuperscript{120} reported on HRTEM experiments on similar MoS\textsubscript{2} samples and some years later published a work on superconductivity in ultra-thin NbSe\textsubscript{2} layers (thickness below 30 Å).\textsuperscript{121}

Here, we studied two members of this group namely hexagonal boron nitride and molybdenum di-sulfide. Latter belongs to the transition metal dichalcogenides (TMD) with structural formula $\text{MeX}_2$ where Me stands for transition metals like Mo, W, Ti and X for chalcogens (e.g. S, Se, Te). TMDs have attracted considerable attention because their electronic properties vary from metals to wide-gap semiconductors and this is expected to hold true also for their 2D phases. This makes them promising candidates for the fabrication of semiconducting devices where for graphene, the absence of a band-gap is a huge problem. In MoS\textsubscript{2} the band-gap changes from indirect (1.2 eV\textsuperscript{122}) to direct (1.8 eV\textsuperscript{123}) during the exfoliation but most important it remains a semiconductor and the potential of single-layer MoS\textsubscript{2} transistors has been demonstrated by Radisavljevic et al.\textsuperscript{124}

Mechanical exfoliated samples are excellent for proof of principles studies and usually they offer the highest crystal quality. However the use for device fabrication is rather limited. Hence alternative synthesis methods like chemical separation of bulk crystals (e.g. via intercalation) or the direct growth of 2D layers on surfaces from gas phase or via phase transformation/separation are highly required. As for graphene, chemical vapor deposition turns out to be very promising also for the synthesis of other 2D materials. Interestingly, besides synthesizing high quality, large area single layers, CVD can be used to grow BN-
Graphene and MoS$_2$-Graphene heterostructures as demonstrated by Shi et al.$^{125}$ and Liu et al.$^{126}$ In this work we found a similar heterostructure, a two-dimensional silica glass on top of graphene,$^{110}$ that, even more astonishing, does not have a bulk counterpart.

### 5.1 Single-layer hexagonal boron nitride

Single-layer hexagonal boron nitride ($h$-BN) has attracted tremendous scientific interest during the last years - mainly as a ultra-flat substrate for graphene as it increases the electron mobility. Besides the structural similarity to graphene (except for the two sub-lattices being occupied by different atomic species and the slightly bigger lattice parameter) there are fundamental differences between $h$-BN and graphene: The atoms are bonded ionic, multi-layers are AA stacked, with boron on top of nitrogen and, most important, single-layer $h$-BN is a wide band-gap semiconductor ($> 5\text{eV}$). Especially latter makes the material very interesting for sandwich structures where one or more graphene layers are separated by a well defined number of insulating BN layers e.g. to study the electronic coupling$^{127, 128}$ or to passivate graphene against the environment.$^{129}$ Consequently, basically all questions that were and are still raised for graphene are exploited for $h$-BN as well, including the structure and role of point defects,$^{130}$ dislocations and grain boundaries,$^{131}$ electrical engineering via doping,$^{132}$ chemical synthesis methods,$^{133, 134}$ other allotropes,$^{135}$ and many more.

Most important, the preparation of single-layer $h$-BN via mechanical exfoliation of the bulk material as well as the transfer to arbitrary substrates such as perforated TEM grids follows exactly the same route as the graphene preparation.$^{136}$ In practice however it turns out to be much more challenging as we did not have access to high quality $h$-BN crystals.$^{137, 138}$ Instead the starting material was a very fine grained powder from which only very small flakes, only a few microns in diameter, can be exfoliated. This complicates the optical identification. As a consequence the thin areas that are transferred to the TEM grid usually are not mono-layers. However, the first HRTEM studies on this materials showed that high-energy electron irradiation can be used for further thinning.$^{27, 139, 140}$ By this, it is possible to produce very small patches of mono-layer areas (a few nm in diameter). Most interesting, these experiments revealed the formation of peculiar triangular holes contrary to the round holes observed for graphene, as can be seen in figure 5.1 (a).

Even though reported differently,$^{139, 88}$ we found that, due to the ionic bonding, it is not possible to distinguish between the boron and the nitrogen sub-lattice in mono-layer $h$-BN at our experimental resolution in TEM mode even if $\Delta Z = 2.$$^{A1}$ This experimental result is nicely reproduced in simulations once charge redistributions are taken into account.$^{A1, A2}$ The isolated atom model (where all atoms are assumed to be neutral) suggests that the nitrogen has 10% stronger contrast as compared to the boron sub-lattice. In the DFT based simulation however, the boron atoms are charged slightly negative. This results in stronger shielding of the core potential, weaker scattering of the high-energy imaging electrons and correspondingly reduced contrast in the final TEM image and vice versa for the nitrogen atoms. By this the contrast difference between the two sub-lattices is reduced to 3% what is beyond our experimental precision. The predicted contrast for IAM and DFT is indicated on the right hand side of figure 5.1. In addition, the contrast ratio between the two sub-lattices can be influenced by residual aberrations as well. Hence it is of enormous importance to account for these effects in the interpretation of the experimental data. This
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It turned out to be a very difficult task because it requires to separate the total contrast into contributions due to the sample and others resulting from imperfections of the optical system. In principle this is possible by making two independent measurements and vary one of the two parameters. Thereby the aberrations can practically not be accessed on the required level of accuracy but one could think of rotating the specimen by a few degree within the object plane. Alternatively, the BN sample could be exchanged with a graphene sample for which each asymmetry in the contrast can be attributed to residual aberrations because the two sub-lattices are identical. In the case of h-BN a double-layer region can serve for this purpose as well because boron is stacked on top of nitrogen resulting in identical projected atom columns. In addition the fact that the aberrations are slowly varying over the field of view offers the possibility to extrapolate the measured aberrations from the double layer regions to the mono-layer areas (that were of main interest here) instead of moving the sample. The required experiments and analysis were developed and performed by J. Meyer. For more details see supplementary informations of ref.A1

Figure 5.1: HRTEM on hexagonal boron nitride. (a) Micrograph shows triangular defects in thin h-BN sheets. (b) Colored image visualizing the asymmetry in the contrast of the two sub-lattices. For double-layer regions this can fully be addressed to residual aberrations of the imaging system. Dashed lines indicate a trend line along which the contrast of the single- and double-layer areas was analyzed. Please note that the aberrations vary slowly over the field of few as compared to atomic distances. (c) Zoom in into the areas indicated by solid lines in (b. (d) intensity line-scans from the same position. In stark contrast to the prediction by the independent atom model we find approximately the same contrast variation for single and double layer regions.

From these very carefully analyzed experiments and in perfect agreement with the DFT based simulation, we conclude that, due to the ionic nature of the lattice, we are not able to address the sub-lattices to boron or nitrogen from the observed contrast. Consequently, these experiments denote the first measurement of the effect of chemical bonding in HRTEM images for a crystalline object. The addressing of the two sub-lattices is possible of course by means of electron energy loss spectroscopy and annular dark-field STEM imaging (where the contrast is much more sensitive to the atomic number) as was impressively demonstrated by Suenaga et al.21 and Krivanek et al.18 An alternative possibility is to make use of the different damage behaviour of boron and nitrogen under high energy electron irradiation that might originate either from the difference in atomic mass or from the different valance electron configuration (different chemistry). From detailed simulations on pristine and defective h-BN configurations in various charge states
in combination with experiments performed at different voltages, Kotakoski et al.\textsuperscript{64} concluded that the peculiar triangular defect formation originates from the difference in the displacement thresholds for B (88kV) and N (130kV) atoms. As a consequence, edges are predominantly nitrogen terminated.

### 5.2 Single-layer MoS\textsubscript{2}

We started to explore the preparation of single-layer MoS\textsubscript{2} from mechanical exfoliation of a natural crystal (spi supplies 429MM) in the framework of a bachelor thesis of Jennifer Gosener.\textsuperscript{141} We did not face unexpected challenges. It is possible to cleave the samples and identify them optically.\textsuperscript{142, 143} We found that a plasma cleaning step of the substrate prior to the exfoliation helps to increase the lateral size of the flakes.

At that time first TEM results have been published by Brivio et al.\textsuperscript{144} In perfect analogy to earlier experiments performed on single-layer graphene,\textsuperscript{145} from electron diffraction as a function of the specimen tilt angle, they were able to show single-layer MoS\textsubscript{2} is not completely flat but has an intrinsic waviness. Importantly they demonstrated how to use the relative intensity of the \{11\textsubscript{0}0\} lattice reflexions to identify single layers. In addition, they performed HRTEM experiments employing an electron energy of 200kV where they achieved lattice resolution in an uncorrected microscope and did not report structural modifications due to beam damage. From our experience on other 2D materials this is very astonishing, especially because DFT simulations on the irradiation hardness determine the displacement threshold to be 90keV for sulfur and 560keV for molybdenum atoms where the sulfurs in the upper layer (facing towards the electron gun) are much more stable as their ballistic ejection is hindered by the lower layers.\textsuperscript{A7} However, after a vacancy is created in the bottom layer, the threshold energy for the top S atom is reduced to similar magnitude as for the bottom layer and thus formation of vacancy columns should be possible even at 80 kV when lattice vibrations are taken into accounted. Hence, under continuous electron irradiation at 80kV (or higher), we expect to observe an increasing number sulfur vacancies. In contrast to Brivio et al.\textsuperscript{144} that was exactly what we observed in our first HRTEM experiments on single-layer MoS\textsubscript{2}.

In combination with HRTEM simulations we were able to identify single and double sulfur-vacancies where sulfur atoms in either one or both layers were removed as shown in figure 5.2(b)-(f). We also found examples of the inverse process - the vacancy filling - as shown in figure 5 of ref.\textsuperscript{A7} This opens a route towards engineering of the electronic properties by means of local substitutional doping. For various substitutions, in MoS\textsubscript{2} and other transition metal dichalcogenides the local density of states along with the substitution energies is given in figure 5 of ref.\textsuperscript{A7} As can be seen, it is possible to introduce mid-gap states in single-layer MoS\textsubscript{2} where N, P As and Sb act as acceptors whereas F, Cl, Br and I atoms behave as electron donors. The implantation of specific atomic species may be possible by controlling the composition of the gas atmosphere as well as the surface migration both of which should be possible in principle but was not targeted in our studies so far. First experiments in this direction where carried out by Wei et al.\textsuperscript{146} They were able to dope BN nanostructures with carbon via high energy electron irradiation while offering an in-situ carbon source in form of a drop of paraffin wax on an piezo manipulator.
5.2 Single-layer MoS$_2$

Figure 5.2: Defect creation in single-layer MoS$_2$ under high-energy electron irradiation. (a) DFT based sputtering cross-section for lower layer of sulfur atoms for static lattice (dashed) and including lattice vibrations (solid). Under continuous 80keV electron irradiation we expect to observe an increasing number of single and double sulfur vacancies structure. Models and IAM based HRTEM simulations created with the QSTEM software of the two vacancy structures are shown in (b)-(e) and experimental example are shown (f). (g) HRTEM images of single-layer MoS$_2$ after an electron dose of $3 \times 10^6 \text{ e}/\text{nm}^2$, $3 \times 10^7 \text{ e}/\text{nm}^2$ and $3 \times 10^8 \text{ e}/\text{nm}^2$. An increasing number of defects can be observed and for very high concentrations point defects start to agglomerate into lines.

From counting the missing sulfurs as a function of the applied electron dose we estimated the sputtering cross-section to be 1.8 barn$^\text{A7}$ what is in reasonable agreement with the theoretical value of 0.8 barn calculated by DFT including corrections due to lattice vibrations as described in section 3.1.1. The first experiments were difficult to analyze because the damage formation was extremely fast. In order to get more reliable results, we reproduced this sputtering experiment at strongly reduced electron fluxes as shown in figure 5.2 (g). Under these conditions we find an even higher discrepancy in the sputtering cross-section ($\approx 8 \text{ barn}$). From newer experiments on MoS$_2$-graphene heterostructures discussed in section 6.2 we learned that our initial interpretation was not correct because the damage in this material can not be addressed only to sputtering. The fact that the damage can be minimized by covering the beam entrance surface with graphene as shown in figure 6.4(b)
indicates that pyrolysis or chemical damage play an important role in the defect formation in free-standing single-layer MoS$_2$ under 80kV electron irradiation.

In addition we found an extremely high initial defect concentration of approximately 1-4% sulfur deficit (of the total number of sulfur atoms) that can not be explained by sputtering. On possible origin is the preparation process - either from the chemicals involved in the transfer or the exfoliation itself. As latter can not be avoided we varied only the transfer by using a PMMA support to mechanically remove the flake and the grid from the substrate instead of etching the glass with KOH.$^{141}$ However this did not influence the number of vacancies. Alternatively, the defects may be present already in the natural bulk crystal - probably in form of sulfurs substituted by other light atoms such as oxygen that would be sputtered rapidly. In section 6.2 we present HRTEM experiments on single-layer MoS$_2$ sandwiched between two graphene layers. In this configuration we do not observe a high concentration of point defects albeit the exfoliation and transfer procedures are identical. Hence it likely originates from impurity sputtering.

Figure 5.3: Formation of line defects in single-layer MoS$_2$ under 80kV electron irradiation. Line defects, unlike isolated point defects, result in highly anisotropic lattice strain. As a consequence, the orientation of the lines depends on the relaxation geometry. At the edge of the free-standing single-layer MoS$_2$ sheet strain can easily be released by deformation of the edge and the lines are predominantly oriented parallel (right). In contrast no preferential orientation is observed in the center of the film (left) where the strain can not be released easily.

Under continuous irradiation the initial sulfur deficit is further increased and the isolated point defects are collapsing into more complicated line defects as can be seen on the right hand side of figure 5.2g. The mechanism behind this is likely to be beam induced migration rather than selective sputtering at defect sides. At the same time, under continuous removal of sulfur atoms, the MoS$_2$ membrane starts to shrink laterally. For a clamped membrane, that is fixed to the supporting grid on all sides, the resulting in-plane strain can be high enough to result in cracking of the complete sheet. An example is shown in figure 4 of appendix.$^{A7}$ For partly free-standing sheets the strain can of course be released to the open edges. The experiments indicate that the line defects are orienting towards minimizing the stain as can be seen in figure 5.3. Vice versa, this may be used to control the orientation by supporting a special relaxation geometry - e.g. by patterning the
membranes prior to the creation of line defects. The energetics and underlying mechanism of the line formation is discussed in more detail in appendix.\textsuperscript{A8}

5.3 2D silica on graphene

Very thin silicon oxide crystals are of interest both for technological purposes as well as for fundamental research. They can overcome many experimental difficulties of bulk SiO\textsubscript{2} such as surface charging and heating\textsuperscript{147} and films with a thickness of a few nanometres have been deposited on metal surfaces.\textsuperscript{148,147} The existence of crystalline 2D silica has first been reported by Löffler et al.\textsuperscript{29} in 2010. They were able to synthesize this new material with a thickness of only 4.2\textgreek{A} on a Ru(0001) single-crystal by means of molecular beam epitaxy performed under UHV conditions followed by a subsequent high-temperature annealing step. They combined scanning probe microscopy, photoelectron- and infrared spectroscopy along with first-principles simulations to identify the film to be formed from two layers of corner sharing SiO\textsubscript{4} tetrahedra bonded together by a linking oxygen.\textsuperscript{29} About one year later the same group reported the first synthesis and atomic scale structural characterization of the amorphous phase of the same material that is obtained by by-passing the crystallization process via rapid cooling after the high-temperature annealing.\textsuperscript{30}

Even before the very first publication by Löeffler et al.,\textsuperscript{29} in HRTEM experiments on CVD graphene, we found a very interesting glass-like adsorbate layer shown in figure 5.4. The material was synthesized by accident during the CVD growth of graphene on copper foil and most likely results from a contaminant in the growth furnace. In the following, we will demonstrate how we could identify the 3D structure (in-plane and out-of-plane) and composition of the adsorbate layer by combining different TEM methods (such as HRTEM/STEM, electron diffraction, analytical EELS, EDX, quantitative ADF and discrete tomography) along with first principles calculations. We will find, that the adsorbate layer is the same 2D silica film consisting of a double-layer of (SiO\textsubscript{4})\textsuperscript{2−} tetrahedra reported by Löffler et al.\textsuperscript{29} and Lichtenstein et al.\textsuperscript{30}

Furthermore, we will discuss in detail the similarities in the defect formation in 2D silica as compared to defects found in single-layer CVD graphene. Finally, and most astonishing, in section 5.3.5 we demonstrate that the most essential transformation is possible and observable in the silica under electron irradiation: The Stone-Wales transformation that for graphene was discussed in section 3.1.2.

5.3.1 In-plane structure and composition

An overview of the sample is shown in figure 5.4. Large areas of the CVD graphene sheet are covered by an adsorbate layer as can be seen in the dark-field image shown in figure 5.4(a). From the HRTEM images we find that the adsorbate, in this experiment, is supported by double layer graphene and the structure is very similar to the amorphous two-dimensional carbon shown in figure 4.5 with a much larger lattice spacing of 4.6\textgreek{A}. The large lattice spacing along with the much stronger contrast (compared to graphene) suggests that the material is a compound built from at least two atomic species one of which we detect because the atomic number is larger compared to carbon.
HRTEM image contrast is excellently suited for structural investigations but it is very difficult to get information on the composition and the bonding environment. For these tasks high-resolution scanning transmission electron microscopy (HR-STEM) is much more powerful due to the strong Z-contrast and excellent EELS capabilities. Hence, for further characterization of the adsorbate, we started a cooperation with David Muller from Cornell university where experiments were performed at a probe-corrected Nion UltraSTEM microscope operated at 60kV. We participated in the experiments but microscope operation and data analysis were carried out by Pinshane Huang.

An overview of the STEM results is shown in figure 5.5. As expected, the layer shows very strong contrast in the low-magnification as well as in the high-resolution ADF images shown in panel (a+inset). The main advantage however were the outstanding possibilities of spectrum imaging: From the EELS spectra we can identify the adsorbate layer to be built from silicon and oxygen atoms where the underlying graphene of course contains carbon. This validates the initial guess that it is a composite material. Moreover, the Si-L\(_{2,3}\) edge structure is very similar to bulk SiO\(_2\) (see green reference in panel 5.5(b) \)). This is a strong indication that the Si atoms are located in a tetrahedral (SiO\(_4\))\(^2-\) bonding configuration. In addition, the carbon K-edge is consistent with bi-layer graphene and does not indicate any covalent bonding between carbon and oxygen atoms.\(^{10}\)

From this we can conclude that the adsorbate lattice is a silica built from SiO\(_4\) tetrahedra forming a planar network that is bonded to the graphene only via van der Waals forces. A model of the projected crystal structure is shown in figure 5.5 (d). The strong contrast observed in HRTEM arises from the more massive silicon atoms. The bridging oxygens are not resolved.
5.3 2D silica on graphene

Figure 5.5: 60kV STEM imaging and spectroscopy of the adsorbate layer. (a) low- and high magnification ADF-STEM images. Due to the good Z-contrast, the layers can found easily and lattice resolution is obtained. (b) EELS concentration maps of Si, C and O proving that the network observed in ADF and HRTEM is build from silicon atoms. Please not that the atomic structure is resolved in the Si map. (c) extracted spectra along with reference spectra for SiO$_2$. (d) in-plane model of a 2D SiO$_2$ crystal on graphene where silicon vertices are connected via bridging oxygen atoms.$^{10}$

5.3.2 Out-of plane structure

In the previous paragraph we gained very detailed information on the in-plane structure of the material. In the following, we want to focus on the information content on the out-of-plane structure (along the optical axis). Three different structures of silica on graphene with identical in-plane projections are shown in figure 5.6(a-c). Model (a) and (b) are very similar: A hydrogen terminated mono-layer of silica tetrahedra where the position of the hydrogens is either altering or all pointing to the same side. These two structures are very similar and extremely difficult to distinguish but having in mind the relatively low structural in-plane order of the material they are the natural choice. With respect to this the third candidate, the bi-layer structure is very different. The thickness is doubled and reproducing the structures observed by HRTEM (e.g. figure 5.4(d)) requires low in-plane order but perfect order of the two layers in z-direction.

Once the composition is known, information on the thickness of the material is naturally contained in the absolute intensities of the detected signals, such as absolute diffraction, absolute EELS and absolute ADF intensities. However, even-though the thickness of the ML and DL structures differ by a factor of two, an interpretation on the required level of accuracy is extremely challenging. Thereby the thickness of the underlying graphene film can easily be determined (from the ADF intensity or from counting the number of steps from a vacuum region$^{66}$) and can be used for calibration.$^{149}$ Further differences between the proposed ML and DL structures are the chemical environment of the bridging oxygen atoms. This difference is reflected in the oxygen EEL near edge structure as found by first principles simulations.$^{10}$

We checked all the above proposed possibilities (except the diffraction intensities) and all of them are pointing towards the DL structure as discussed in detail in the supplementary information of ref.$^{10}$
Finally the thin silica films are excellent candidates for HR-TEM tomography. The experiments did strongly suffer from the relatively low stability of the material under 80kV electron irradiation. However, we found an area where the graphene along with the covering silica film was flipped over, allowing an edge-on view of the structure as shown in figure 5.6 (d-f). This can be thought of as a discrete tomography experiments (with two rotation angles 0° and 90°). The two extra lines of the silica observed in the 90° projection are a strong evidence for the double-layer nature of the film.

Figure 5.6: Out-of-plane structure of the silica film on graphene. (a-c) three models of silica on graphene with identical in-plane structures (shown in figure 5.5(d)) but different out-of-plane structure. (a) and (b) hydrogen terminated monolayers of silica tetrahedra and (c) double layer where two layers of tetrahedra are connected with an edge sharing oxygen. (d) HRTEM edge-on view of folded silica on graphene coloured rectangles are magnified in (e) and (f). Three dark lines arise from the triple-layer graphene substrate (blue arrows) and two additional lines (highlighted by red arrows) that prove the double-layer nature of the silica film and rule out the mono-layer models shown in (a) and (b).

By combining different TEM techniques we were able to resolve the full 3D structure and composition of the adsorbate layer and found that the material is exactly the same as the 2D silica film reported on Ru(0001). Remarkable differences however are:

1. The lattice mismatch between the SiO$_2$ and the substrate. The SiO$_2$ lattice parameter is 5.3Å (5.42Å reported in ref$^{29}$) that is roughly 2.14 times that of graphene but exactly 2.0 times the one of Ru(0001) resulting in a mismatch of 0% and 7% for Ru
and graphene respectively.

2. On Ru, there are indications of bonding of the oxygen to the substrate\textsuperscript{29} what we do not observe on graphene as evident from the carbon k-edge structure.

As a consequence, in contrast to Ru where the orientation of the crystalline areas coincided with the lattice directions of the Ru support,\textsuperscript{30} we did not observe any epitaxial relationship between the crystalline areas and the underlying graphene. Still, DFT simulations show that the van der Waals interaction to graphene energetically stabilizes the 2D structure with respect to bulk SiO\textsubscript{2} (for more detail see supplementary information of appendix\textsuperscript{A10}). This indicates a new class of 2D materials that do not have a bulk counterpart but do form only on surfaces.\textsuperscript{A10}

### 5.3.3 Atomic scale analysis of the amorphous phase

So far we determined the composition and the crystal structure of the before unknown adsorbate. In the following two sections we will have a detailed look into the amount of ordering in the 2D silica as well as into its defect assignment. We will find striking similarities between defects in crystalline 2D silica and defects found in CVD graphene.

If we again have a look at the HRTEM image shown in figure 5.4(d), we notice that the atomic order in not very high. Still, atomic resolution imaging that usually is hindered for unordered systems by the projection problem,\textsuperscript{150,151} is enabled by the 2D nature of the material. Interestingly, the overall structure is neither crystalline or nano crystalline nor fully amorphous. However the structure of the silica strikingly resemble Zachariasen’s cartoon models of a 2D continuous random network glass from 1932,\textsuperscript{28} as shown in figure 5.7.

![Figure 5.7: a,b) Zachariasen’s model of atomic arrangements in glass. c,d) Experimental HRTEM images of silica glass on graphene. e,f) Nano-beam electron diffraction pattern of crystalline and amorphous silica glass (indicated by blue arrows and rings) on multilayer turbo-stacked graphene (overlayed by yellow ring).](image-url)
Consequently, this, and the work done by Lichtenstein et al., are the first atomically resolved structural images of a glass - precisely 80 years after Zachariasen draw his famous structure models. Just recently, an interesting review on the research activities on random networks from that time until now was published by Wright and Thorpe.

The interest into these structures, however, goes far beyond the field of solid state physics. Weaire and Rivier, in their paper "Soap, Cells and Statistics - Random Patterns in Two Dimensions" stated that "all natural structures (and many artificial ones) represent some compromise between order and chaos". The ordered state represents the regime of crystals. When disorder predominates in the solid, however, it is often termed glass or amorphous. Moreover, they point out that, looking beyond physics, such non-ideal structures are the rule rather than the exception.

"Biological cells, geographical or ecological territories and other natural structures on scales much greater than molecular dimensions are usually disordered. ... Even the bee’s honeycomb is not as perfect as has often been supposed (Wyman 1865). ... If the need for a proper theory of random structures is so obvious, how have the adherents of the various scientific disciplines responded to it? Condensed-matter physicists have tended to ignore questions which lie far outside the range of equilibrium statistical thermodynamics, and to study disorder only in that context. Recently, however, there has been a growth of interest in disorder over a wider field-percolation theory, chaos, fractals-as well as the work of the amorphous solid-state community to which we have already referred."  

Because it is extremely difficult to study disorder in three dimensions, Weaire and Rivier are focusing on two-dimensional structures that they loosely classify as cellular such as the network formed by foam bubbles. Some examples are shown in figure 5.8. Even though the length scales of foam bubbles (mm), cells (µm) and a 2D silica film (nm) differ by many orders of magnitudes the formed network structures show striking similarities and identical classifications can be used for their description.

Astonishingly, we even find a one-to-one correspondence between processes exemplified for
cells by Weaire and Revier (shown in figure 5.9) and processes observed in our HRTEM experiments on graphene: Stone-Wales transformation (bond rotation) represents an elementary local rearrangement (T1 process), sputtering is equivalent to vanishing of cells (T2 process) and the analogue of cell divisions (mitosis) is the inclusion of ad-atoms. Most remarkably they even explain the creation of a dislocation dipole in a hexagonal cellular structure by subsequent mitosis steps (inclusion of extra row of cells). This represents exactly the inverse process of the dislocation creation via sputtering (removal of on atomic row) that we observed and discussed for graphene in section 4.3.

Figure 5.9: (a-c) Elemental processes in random networks exemplified for cells. (a) Elemental local rearrangement [153, Fig. 2]. (b) Vanishing of a cell [153, Fig. 3]. (c) Cell division [153, Fig. 4]. (d) Creation and dissociation of a dislocation pair by successive cell divisions [153, Fig. 6]. In graphene the corresponding processes are Stone-Wales transformation, sputtering and the inclusion of adatoms. The inverse process of (d), the annihilation of two dislocation dipoles via atom removal is shown for graphene in figure 4.9.

In Zachariasen’s model, amorphous and crystalline structures differ only by allowing for variable bond angles. This maintains the local chemical order while introducing structural disorder. Similar to a foam bubbles, the atoms in amorphous materials built a network of rings of various sizes and orientations. If, e.g. foam bubbles are constricted to two dimensions, as can be done by two glass plates, a planar ring-network is formed. The same is the case for the 2D silica. This allows to obtain atomic resolution images in transmission mode by by-passing the projection problem and for the fist time opens the possibility to directly extract atomic positions of this vitreous material. Tracking nearest neighbor positions of silica atoms reveals the full network structure and offers access to fundamental statistical quantities such as ring-statistics, Si-Si bond-length and bond-angles as well as the radial distribution- (RDF) and higher order Si-Si correlation functions. Ring-statistics are of great interest as they allow to differentiate between structures with identical RDFs. Here 2D materials, at the moment, offer the unique possibility to directly compare ring-statistics obtained from experiments and simulations as this quantity can not be accessed by any experimental method for bulk materials, so far. The results of our statistical analysis are presented and discussed in detail in appendix.
5.3.4 Point defects and grain boundaries in crystalline areas and the similarity to graphene

In the last paragraph we found that the 2D silica film that was synthesized on graphene does have a glass-like structure where both, the crystalline and the vitreous state have been reported on Ru(0001).\textsuperscript{29,30} From the work by Lichtenstein et al.\textsuperscript{30} we know that the amorphous phase is metastable because the crystal is lower in energy. Moreover, depending on the cooling procedure in their synthesis they are able to end up with either one or the other configuration. This proves that the transition from the metastable to the crystalline phase is possible and does happen given, that the system has enough time to relax during cooling (low cooling rate). As our synthesis happened accidentally we did not have the possibility to control or to vary the cooling-rate. However, we observed highly crystalline areas in the regions where Raman mapping was performed. We expect that the transformation was possible due to high heat input of the focused Raman laser. This idea is further supported by the fact that it was easily possible to detect the areas where the Raman mapping was performed by the smaller thickness of the supporting Quantifoil film indicating that the heat input was sufficient to burn the carbon film.

![Image of Nano-crystalline SiO$_2$ on graphene after laser heating.](image)

Figure 5.10: Nano-crystalline SiO$_2$ on graphene after laser heating. (a) HRTEM overview image. (b) selected area electron diffraction pattern from a region of approximately 100nm in diameter. (c) HRTEM at higher magnification with maximum filter applied and polygons overlaid in (d). The crystalline regions show a distinct 30$^\circ$ degree grain angle as can be seen from the FFT and are predominantly connected by 5-7 grain boundaries.
Figure 5.10 shows an overview of the SiO$_2$ film on graphene after the laser heating. From the HRTEM image (5.10(a)) and the selected area diffraction pattern (5.10(b)) it is obvious that amount of order increased dramatically as compared to the earlier experiments shown in figure 5.4(d), 5.5(a) and 5.8(d). The resulting film should be characterized as nano-crystalline rather than amorphous. This is especially pronounce by comparing the diffraction patterns shown in figure 5.10(b) with the one from the initially unordered film shown in figure 5.7(f).

The polycrystalline silica film is formed from highly crystalline grains with grain diameters in the range of 10 nm that are connected by grain boundaries that predominantly are formed from pentagon-heptagon pairs. Most interesting, the grains tend to form a 30° degree angle and are connected by twin boundaries that, in perfect analogy to the grain boundaries in CVD graphene discussed in section 4.2, take on locally curved configurations. Rarely, we also observe 5-5-8 grain boundaries in the 2D SiO$_2$ that were reported for graphene as well$^{156}$ but were never observed in the graphene layers studied here. Figure 5.11 shows a comparison between the grain boundaries in silica and graphene.

![Figure 5.11: Grain boundaries in 2D silica. (a) HRTEM overview image of the silica film with two different types of grain boundaries marked and shown in more detail in (b) and (e). Predominantly they are formed from a chain of pentagon heptagon pairs as shown in the top row where (b) is for 2D SiO$_2$, (c) for graphene (discussed in more detail in section 4.2) along with a structure model shown in (d). The lower row shows an example of a 5-5-8 grain boundary in silica (e) and graphene (f). The STM image shown in (f) is taken from Lahiri et al.$^{156}$ as this GB configuration does not appear in our CVD graphene samples (Reprinted from [156, Fig. 3], ©2010, with permission from Nature Publishing Group). Scale bar 5 nm (a) and 2 nm (b,c,e,f).](image)

In addition to the grain boundaries, the silica film contains a very high density of point defects as shown in figure 5.12. We think that most of them are compensating the higher atom density of the unordered film (as reported by Lichtenstein et al.$^{30}$ ) and consequently are of an ad-atom type. One very clear example of an isolated double ad-atom configuration in a pristine part of the silica lattice is shown on the right hand side of figure 5.12. Consequently, vacancy type defects such as double-vacancies should be very rare. So
far however, we can not make any conclusion whether one or the other type is observed more frequently as the defects do not tend to be isolated but often form complex defect structures that are difficult to analyse. This information of course would be interesting as it is not clear if the atomic density remains constant during the crystallization or if the film is simply expanding or tetrahedra can be released to the surface. After intensive searching we found some nice examples of (at least almost) isolated vacancy type defects. Most astonishing however is the huge number of flower defects. The overview image shown in figure 5.10(a) already contains 8 examples of perfect flower defects. As discussed earlier, this defect is a purely structural defect that has the same atom density as the crystalline lattice. A second member of this type is the Stone-Wales defect that is observed as well and will be discussed in more detail later.

<table>
<thead>
<tr>
<th>Stone-Wales</th>
<th>Flower</th>
<th>Double Vacancy</th>
<th>Double ad-atom</th>
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<tbody>
<tr>
<td><img src="image1" alt="Stone-Wales" /></td>
<td><img src="image2" alt="Flower" /></td>
<td><img src="image3" alt="Double Vacancy" /></td>
<td><img src="image4" alt="Double ad-atom" /></td>
</tr>
</tbody>
</table>

Figure 5.12: Comparison of isolated point defects in 2D silica and single-layer graphene. Stone-Wales and flower defect shown in (a) and (b) are purely structural defects with an atomic density identical to the pristine lattice. In contrast the vacancy (c) and ad-atom (d) type defects show density deficiency and excess respectively. Please note that the for the double vacancy we show two examples where for the more complex one on the right hand side the atomic configurations are very similar but not exactly identical for the silica and the graphene. For direct comparison all images (except SW) are displayed at the same magnification. All scale bars are 1 nm.

In figure 5.12 we compare the different kinds of point defects in silica and graphene. Please note that for direct comparison they are displayed on the same scale. We find a perfect analogy in the defect formation except that the silica lattice constant is bigger by a factor of 2.14.
The similarity between the two materials can easily be understood within a rigid-unit-model\(^\text{157}\) where the carbon atoms in graphene are replaced by the double tetrahedral unit building up the 2D silica. For a silicon tetrahedra a rigid-unit-model is suitable because the "the force constants associated with stretching of the Si-O bonds and bending of the O-Si-O bond angles are much stronger than the interaction between neighbouring tetrahedra (e.g., Lasage and Gibbs 1987, 1988), such as the force constants for bending of the Si-O-Si bond angle."\(^\text{157}\) If we assume that the basic unit (for the 2D silica these are two tetrahedra) is perfectly rigid, its internal structure can be neglected completely and the 3D structural arrangement is determined only by the nature of the interaction between neighbouring units - namely by the length and the stiffness of the Si-O-Si bond. Hence, the similarity between the defects in graphene and the silica film originates from the similarity of the bonding between two tetrahedra and two \(sp_2\) hybridized carbon atoms.

This is by no means true for all types of tetrahedral units as they can bond either corner- or edge-sharing. For a range of materials the tendency of the MXM bond angles in an MX\(_2\) melt is shown in figure 1 of ref.\(^\text{158}\) As can be seen SiO\(_2\) is on the side of extremely corner sharing. For materials with more flexible bond angles, such as GeSe\(_2\) or SiSe\(_2\), we also expect more flexibility in their defect production. Consequently, they should be more versatile and loose the similarity to the defects in graphene as the \(sp_2\) C-C bond is a very directional bond.

### 5.3.5 Stone-Wales transformations

Besides the similarities in the defect configurations we observed the most fundamental defect transformation under electron irradiation also for the 2D silica - namely the Stone-Wales transformation that for graphene we discussed in detail in section 3.1.2. Figure 5.13 shows, step-by-step, an inverse Stone-Wales transformation (5.13(a)+(b)) along with two examples of the appearance of two such defects in an initially pristine area (5.13c).

![Stone-Wales transformation in 2D SiO\(_2\).](image)

**Figure 5.13:** Stone-Wales transformation in 2D SiO\(_2\). (b) inverse Stone-Wales transformation in unordered silica. Small panels show intermediate configurations and (a) shows an overview where the SW defect is marked by the white box. (c) two examples of SW transformations in crystalline silica. The upper row: original HRTEM micrographs and lower row with maximum filtering applied for better visibility of the defect structures.
For graphene, these electron beam induced bond rotations can simply be explained by knock-on events where one of the two atoms gains energy and momentum from an electron. As the target atom is still chemically bonded to the graphene, part of the energy is transferred to the neighbouring carbons during the ejection. From first glance, this seems to be the case for the silica as well. However instead of two carbon atoms now two double-tetrahedra are changing their positions with a total of 4 sulfur and 12 oxygen atoms being involved. Hence, it is difficult to imaging that a single knock-on event can be responsible for this transformation. Moreover, the two SW defects in figure 5.13(c) happen to appear at the same time. Hence, in-plane strain likely plays an important role in the SW transformation in 2D silica. Most likely the films are highly strained in our experiments as they are shrinking under continuous electron irradiation. Still, knock-on events may be important to trigger the transformation in strained silica.

Besides the question why SW transformations can be observed, it is of great interest how the atoms are rearranging. Can the observed dynamics be understood within a rigid-unit-model where the single or even the double tetrahedra stay intact and only undergo translations and rotations or are these building blocks destroyed completely and rebuilt at the new position? With HRTEM we can follow the evolution of the defects in real time as shown in figure 5.13(b). Unfortunately we are lacking the resolution, especially in z-direction as we only see the projected structures, to really directly track the atom positions in three dimensions. However, most likely, they do not follow the simple trajectory schematically outlined by Lichtenstein et al. in figure 4b of ref.30

In conclusion, we were able to prove that the most essential transformation is possible and observable in the silica under electron irradiation. This basically opens the way for e-beam manipulations of defects as shown for vacancies, grain boundaries and dislocations in graphene in chapter 4. Before, it would be beneficial to perform molecular dynamics simulations on the fundamental SW transformation to determine the exact transformation path and clarify the role of in-plane lattice strain.
6 Graphene - An ideal TEM substrate


In contrast to optical microscopy, fully transparent support films do not exist for TEM because electrons are strongly interacting with all kinds of matter. However, the image contribution of the substrate can be minimized by reducing the thickness and the atomic number. Consequently, graphene, with a thickness of only one atomic layer built from very light carbon atoms is as close to vacuum as possible. Specimen on graphene can therefore be imaged as if they were free-standing.

In addition, it has a number of very interesting properties that should positively affect the TEM image acquisition:

- Crystallinity: The HRTEM image contribution of the single-layer graphene support is known precisely. Hence, it can be removed (e.g. by subtraction or by removing the corresponding spatial frequencies with a Fourier filter) to reveal the sample of interest that is deposited on top.

- Semimetal: Graphene can act as a conductive coating to minimize ionization damage. This is especially interesting for insulating samples.

- The good heat conductance of the graphene layer can minimize damage due to local heating by the high energy electron beam.

- Impermeable membrane: Sputtering at the beam exit surface can be avoided by metal coatings.\textsuperscript{159} This effect is expected for graphene as well because it is highly impermeable, as shown for gases by Bunch et al.\textsuperscript{7} By this graphene encapsulation can prevent liquid samples from out-gassing (allowing wet-phase imaging), as demonstrated for bacteria by Mohanty et al.,\textsuperscript{15} and, what is most important here, effectively shields the enclosed sample against residual gases within the microscope vacuum. At the same time, the graphene offers a well defined albeit chemically inert carbon environment.

Consequently, graphene as well as related ultra-thin carbon substrates (such as graphene oxide or SAMs) have attracted considerable attention as TEM substrate for high-resolution imaging and spectroscopic application on biological specimen that naturally are suffering from very weak contrast (without staining) and high electron sensitivity.\textsuperscript{11,13,160,12,15} Some examples are shown in figure 6.1.
6 Graphene - An ideal TEM substrate

6.1 Achievable resolution not limited by the substrate

The benefit of graphene, as compared to standard amorphous carbon films has been demonstrated.\textsuperscript{11,12,160} However, all the above studies were performed at rather low magnifications (and low resolution) what most likely was limited by the stability of the investigated materials. Here we want to explore the potential of graphene substrates for atomic scale imaging and spectroscopy studies in materials sciences. A first example was shown in the previous chapter: The 2d silica glass on graphene again shown in figure 6.2. We find that the graphene substrate is excellently suited for HRTEM imaging and spectroscopy analysis of the silica. Thereby, silicon atoms are clearly resolved indicating a resolution better than 3Å in both imaging and spectroscopy mode as can be seen in figure 6.2 and 5.5(b).

Figure 6.2 contains a second example that can easily be overseen: graphene on graphene. The precise atomic configuration of the grain boundaries in the triple-layer regions are clearly detected after removing the image contribution of the supporting turbo-stacked graphene layers with a Fourier filter. This demonstrates a resolution of $\approx 2\AA$ what is the limit of the machine. Furthermore, the spacial frequencies of the substrate (two layers) and the object (third graphene layer) are identical. This proves the full potential of using graphene as an extremely thin, crystalline substrate for HRTEM imaging and spectroscopy applications. One key requirement for practical realization however is the preparation of high-quality, single-layer graphene films with atomically cleanliness and controlled polarity (hydrophobic/hydrophilic) as discussed in detail in the doctoral thesis of my colleague Gerardo Algara-Siller that will be published soon.

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Figure 6.1: Graphene as ultra-thin carbon support for biological applications. (a) Stained DNA on graphene (Reprinted from [160, Fig. 4], ©2011, with permission from Elsevier). (b) Unstained 20S proteasome on graphene oxide (Reprinted from [11, Fig. 5], ©2010, with permission from Elsevier). (c) Ice embedded TMV virus fragment on conductive carbon nano membrane (heated SAM) (Reprinted from [12, Fig. 6a], ©2011, with permission from Elsevier).
6.2 Minimization of beam damage

In the last paragraph we demonstrated the use of graphene as ultra-thin substrate for high-resolution TEM applications. In the following we want to concentrate on the question if, due to the good thermal and electric conductivity, it can serve to minimize beam damage as was demonstrated for graphene encased bacteria by Mohanty et al.\(^\text{15}\) A very promising lab system for this type of studies are heterostructures of different 2D materials, because they allow direct comparison between free-standing, graphene supported and graphene encased samples. Thereby, more and more complex geometries offer more and more control whereas it is always possible to study each of the building blocks individually. Analysing the relative differences between different experimental setups allows to separate the total damage into contributions of different origins. E.g. already for a two-layered heterostructure, such as MoS\(_2\) on graphene, the sputtering geometry can be changed dramatically by a 180° rotation of the sample: If the graphene is located underneath the MoS\(_2\), it has a very high stopping power for the sputtering from the bottom layer sulfur atoms. This of course is not the case for the tilted configuration. At the same time, the improved thermal and electrical conduction due to the graphene is identical. This allows to separate sputtering from other damage mechanisms. Even more control can be gained from a real sandwich geometry where the MoS\(_2\) is enclosed between two graphenes because, by this, it is possible to control the chemical environment of the sample in addition.

The most important prerequisite for all these investigations is the formation of an atomi-
cally sharp interface between the stacked sheets as reported from cross-sectional HRTEM imaging of multi-layer heterostructures by Haigh et al.\textsuperscript{161} They found that the contamination that is trapped during the assembly of the layers is segregating into isolated pockets and the interfaces between the layers are atomically clean.

![Image](image_url)

**Figure 6.3:** Overview on the preparation of MoS\textsubscript{2} on graphene. First a graphene sample is mechanical exfoliated and identified on SiO\textsubscript{2} (a) and transferred to the TEM grid (b). Then a single-layer MoS\textsubscript{2} sample is exfoliated in the same way and the graphene on the TEM grid needs to be placed on top of the MoS\textsubscript{2} flakes (c)-(d). (e) low-magnification TEM image showing one of the MoS\textsubscript{2} layers on graphene. The selected electron diffraction pattern recorded from the same area reveals that the MoS\textsubscript{2} is single-layer as evident from the altering intensities of the \{1100\} lattice reflexions.\textsuperscript{144} The values indicate the mean diffraction intensity in the marked areas. Furthermore, from the intensity profile of the graphene reflexions (purple), we find that the supporting graphene is at least two layer thick.\textsuperscript{145} (g) HRTEM image of single-layer MoS\textsubscript{2} on multi-layer graphene.
Our first choice was to study the combination of single-layer MoS\(_2\) and graphene at 80kV because MoS\(_2\) it is a semiconducting material and hence may suffer from ionization damage. From our experiments on free-standing MoS\(_2\) layers we learned that at this electron energy the material is not very stable and, most important, we found the damage production to be much more efficient than suggested by the sputtering simulations \((\sigma_{\text{MoS}_2}^{\text{theory}} = 0.8\ \text{barn} \text{ and } \sigma_{\text{MoS}_2}^{\text{exp}} \approx 8\ \text{barn} - \text{ see chapter 5.2})\). Consequently, in addition to knock-on damage other damage mechanisms such as ionization or chemical etching must be present.

The first challenging task is the sample preparation. Although we are aware that chemical routes for synthesis of MoS\(_2\)-graphene\(^{125}\) and BN-graphene\(^{126}\) heterostructures do exist we decided to work on mechanically exfoliated and stacked layers as they offer a much more defined starting point for our investigations (single crystals, known thickness, known position). The production steps for a two-layer structure are outlined in figure 6.3.

A sandwich structure is obtained by adding one more graphene layer. Although we are very experienced in the preparation and transfer of MoS\(_2\) and graphene samples the preparation of heterostructures still is a major technical challenge as it requires a lot of patience in searching the flakes and micron scale positioning of the 2D sheets on the TEM grid. This was successfully performed by Mona Sedighi in the framework of a master thesis.

Figure 6.4 shows a set of four experiments targeting the damage in single-layer MoS\(_2\) under continuous electron irradiation in different sputtering geometries. The free-standing MoS\(_2\) shown in (a) is a semiconducting thin sample that definitely suffers from knock-on damage but potentially from ionization and chemical damage as well and can be used as a reference. As can be seen from the FFT in the lower row, the crystalline order is lost after applying a specific electron dose of \(7.3 \times 10^8 \frac{\text{e}}{\text{nm}^2}\). Placing the graphene on top of the MoS\(_2\) should reduce ionization damage by providing improved thermal and electrical contact of the sample. In the opposite orientation, the thermal and electrical contacts are identical but the sputtering geometry is improved in addition (resulting in increased threshold energy) because the sulfurs are stopped by the graphene layer. Hence the difference between (b) and (c) can fully be addressed to knock-on damage where the difference between (a) and (b) can mainly be addressed to ionization damage. The sandwich structure shown in (d) finally allows to control the chemical environment and may serve to reduce chemical damage (similar to the chemical etching in graphene discussed in section 3.2). As can be seen, e-beam damage in single-layer MoS\(_2\) can practically be avoided completely by graphene sandwiching.
Figure 6.4: Single-layer MoS$_2$ in various sputtering geometries. (a) free-standing, (b) graphene on top, (c) graphene below and (d) sandwiched. HRTEM images in the two lower rows show the initial and final state of the samples after 80kV electron irradiation with a cumulated dose of $7.3 \times 10^8 \frac{e}{nm^2}$ at a constant dose rate of $9 \times 10^5 \frac{e}{nm^2s}$. After this dose the crystalline order is lost for the free-standing sample as can be seen from the FFTs. The damage can be minimized by the graphene layer that offers improved thermal and electrical conduction when placed on top and an improved sputtering geometry when placed below the MoS$_2$. Remember that for the free-standing case only the lower layer sulfurs are sputtered. The sandwich structure allows to control the chemical environment and by this reduce chemical damage. From the last row we find that, sandwiching single-layer MoS$_2$ between two graphene layers, can practically completely avoid e-beam damage under 80kV electron irradiation.
At the moment this is a proof of principles experiment awaiting further analysis and experimental work. However it demonstrates the huge potential of this approach for i) fundamental understanding of e-beam damage and ii) minimization of beam damage. Some very important results can already be drawn now:

1. Graphene dramatically reduces the beam damage in MoS$_2$ under 80kV electron irradiation. Especially in the sandwiched configuration, the material can withstand much higher electron doses. This is very important as the trend in TEM research to obtain quantitative information from smaller and smaller volumes (such as the detection of chemical bonding of point defects, single-atom spectroscopy and tomography) require extraordinarily high electron doses.

2. The discrepancies in the theoretical and experimental sputtering cross-section for single-layer MoS$_2$ discussed in section 5.2 arises because only a small fraction of the total damage can directly be attributed to knock-on.

3. A set of experiments allow to decompose the total damage into contributions from ionization, heating, knock-on and chemical damage.

A very fascinating follow-up experiment, especially with respect to the last point in the above list would be to exchange the graphene layers by other materials. Single-layer $h$-BN, for example, offers the same knock-on protection, similar control of the chemical environment but, in contrast to graphene, it is a wide band-gap semiconductor. Consequently, this would give detailed insight into the role of the electron conductivity of the specimen encasement for the reduction of ionization damage.
6.3 Outlook: Atomic resolution imaging of molecules on graphene

In the last two paragraphs we learned that graphene is an extremely promising substrate for HRTEM imaging and spectroscopy experiments because it minimizes beam damage and does not limit the resolution. These two results raise the hope of atomic resolution investigations of biological samples on graphene.

Hence, we performed first experiments on perchlorocoronene (PCC) molecules deposited on CVD graphene TEM samples by thermal evaporation at 250° in UHV. The samples were prepared by Andrey Turchanin from University of Bielefeld. They verified the presence of chlorine on the samples by X-ray photoelectron spectroscopy (XPS). PCC can be synthesized from coronene by replacing all hydrogens by chlorine atoms. Even though hydrogen free molecules are definitely not typical biological samples we decided to start with PCC as halogenation has proved to be very useful to minimize beam damage because the weakest parts, the hydrogen atoms, are replaced. Moreover, chlorine atoms are much heavier as compared to the carbon support, resulting in much stronger contrast. Hence, their characteristic ring-like arrangement is easily detected. Examples of PCC molecules on graphene along with a simulated HRTEM image is shown in figure 6.5. The simulation shown in figure 6.5(c) was performed with the QSTEM software on a non-relaxed structure of PCC on graphene.

![Figure 6.5: HRTEM of PCC on graphene. (a) structure model of PCC molecule. (b) and (c) show model of PCC on graphene and the corresponding simulated HRTEM image. Therefore the molecule was put on top of single-layer graphene at an arbitrary position (no structural relaxations were performed). (d) overview of the sample with molecules marked by arrows. (e) and (f) HRTEM micrographs of two different PCCs on graphene in top view. (g) shows an example of a molecule standing perpendicular to the graphene sheet.](image-url)
Under the electron beam we observed repeated flipping and discrete rotation of the molecules along the graphene crystallographic directions as can be seen in figure 6.6. This is a very strong indication that the ring like structures are really planar. Even though this is a dynamical and completely unexpected effect, this already is the implementation of a discrete tomography experiment that allows to extract 3D structural informations (similar to the determination of the structure of the silica film from top- and side-view images shown in figure 5.6).

Figure 6.6: Dynamics of PCC molecules on graphene. Interestingly, we observe flipping and rotating of the molecule under continuous electron irradiation. This allows to observe the molecule in side-view, proving that the structures are planar. The molecule pointing out of the plane is always roughly aligned along the graphene arm-chair direction and the rotations are discrete. Numbers on the top indicate the time relative to the first frame and the complete sequence was recorded at a dose rate of $1 \times 10^7 \frac{e}{nm^2 s}$ resulting in a total dose of $1.9 \times 10^9 \frac{e}{nm^2}$.

Most important, our preliminary experiments demonstrate that HRTEM experiments on biological samples deposited on graphene, as well as their preparation, are feasible. In addition we observe completely unexpected dynamics of the molecules and we expect the study of the underlying mechanisms to be an extremely complicated but similarly exciting task. Here, we also want to mention that care in the interpretation must be taken: Alternatively to flipping, the molecule could change the shape from ring- to line-like by opening the chlorine ring and binding to the graphene. Unfortunately it is not possible to distinguish these two possibilities only based on the HRTEM sequences. Hence, in the future, we will perform atomistic simulations to learn more about the energetics of these processes. Before, however, we should go one step back. The dynamics are introduced by the electron bombardment and the electron doses used so far are typical for material sciences but many orders of magnitude higher than typically used in biological applications. Hence, the logical next step will be to focus on structural investigations under dramatically reduced electron flux.

Here we are at a point where two different worlds meet: 1) materials science where high doses are needed for high resolution imaging at precisely controlled imaging conditions (focus, astigmatism) the setup of which is already very dose expensive. (Pre-work on the implementation of low dose acquisition including automated focusing and stigmating algorithms was done by Jens Lechner. His work was targeting dose reduction in electron tomography on carbon materials.) And 2), biological samples where the low stability under electron irradiation and elevated temperatures is dramatically limiting the usable experimental methods in all aspects of TEM research ranging from sample preparation to
image acquisition and data analysis. One speciality is the use of low-dose acquisition and analysis tools where special algorithms are used to track and correlate features in HRTEM time series that are not visible in the single frames due to inherently bad signal-to-noise ratios.

Hence, the goal of atomic resolution structural analysis of biological molecules on graphene by means of HRTEM will require a very good interdisciplinary cooperation. On this route many technical issues need to be tested both on experimental side (e.g. sample preparation, low-dose set-up of appropriate imaging conditions) as well as with respect to the data analysis. Most likely the existing single-particle analysis algorithms need to be modified to be able to work on crystalline objects or substrates. For all these tasks graphene and especially small defects in graphene such as the flower defect or double-vacancy configurations are excellent model systems because they have similar structure, size and composition but are extremely stable, well characterized and easily available. Finally, theoretical modelling of the experimental findings will be needed to gain further insight (e.g. into the molecule flipping). First experimental as well a theoretical work on the dynamics of small molecules on graphene has been done already by Schäffel et al.165
7 Summary and Conclusion

Recent technical advances in TEM optics allow obtaining very high spatial resolution. Even at reduced beam energies of 80kV, needed to avoid knock-on damage in many carbon materials, the performance is sufficient to resolve the carbon lattice atomically. At about the same time, 2D crystals were discovered, which allow to bypass the projection problem in TEM. When combining these two factors, we enjoy for the first time, the possibility to determine the position as well as the dynamics of individual atoms in real time. This opens the route to a huge variety of materials science phenomena that, so far, could not be addressed experimentally. It is just a textbook example of simplifying a scientific question by reducing its dimensionality. Hence, 2D-materials are started to be explored by a steadily growing group of researchers. Thereby a very close cooperation between experimental findings and further development of theoretical modeling turned out to be essential to create fundamental new insights.

In this work we extensively used the combination of 2D materials, aberration-corrected TEM and atomistic modeling to address a variety of materials science phenomena on 0D, 1D and 2D defects in 2D materials. These are:

- Identification, creation and dynamics of point defects (nitrogen substitutions, single- and double vacancies)
- Grain boundary migration in polycrystalline graphene
- Creation, interaction and annihilation of edge dislocations
- Direct imaging of the amorphous state for 2D silica glass and irradiated graphene. For latter, it was even possible to follow, step-by-step, the transition from a 2D single crystal to a 2D amorphous carbon membrane.
- Detection of chemical bonding in HRTEM micrographs as demonstrated for nitrogen doped graphene and single-layer hexagonal boron nitride. For the first time we experimentally demonstrate that HRTEM images contain not only structural information (atomic positions) but information on the chemical state of the system in addition.

Thereby, single-layer graphene turned out to be an ideal model system mainly because of the structural simplicity, its precisely defined thickness, the availability and the outstanding radiation hardness making it extremely stable at reduced beam energies.

In the following I want to give a short overview on the most important findings (the corresponding chapters are given in brackets).

In chapter 3 and 4, we show that it is possible to gain very detailed information on the defect formation, energetics, interaction and dynamics of graphene. It is however by no means a-priori clear whether this directly transfers to better understanding of these questions in bulk materials. For grain boundaries in graphene we find that their dynamics under electron irradiation can be understood by a driving force proportional to $\gamma/R$ where $R$ is the local curvature and $\gamma$ is the GB energy per unit length (4.2). This concept is borrowed from macroscopic GB migration in solids and for this example we find a one-to-one correlation between 2D and 3D.
One peculiarity however results from the extreme flexibility of graphene: Because "the energy from bending the graphene membrane is three orders of magnitude smaller than the energy from in-plane strain," the material easily releases compressive strain via out-of-plane corrugations. In 3D this is strongly suppressed by the presence of neighbouring atomic planes. As a consequence, point defects in graphene do interact not only by strain fields but also via local lattice corrugations as we could show both experimentally and from simulations for the interaction of e-beam induced dislocations (4.3).

Even in the remarkable list above, the atomic scale study of amorphous materials is absolutely outstanding as, so far, this is achieved only for 2D materials. However, the absence of structural order in our surrounding nature is rather usual than exceptional. Hence, the interest into random network structures goes far beyond the field of physics as stated in detail by Weair and Rivier in "Soap, cells and statistics - random patterns in two dimensions". Now, for the first time, it is possible to directly extract atomic position in unordered networks from direct images as demonstrated first for artificially amorphous graphene shown in figure 4.5. In this work, we discovered a 2D silica glass that was accidentally synthesized on top of graphene in a CVD process (5.3). From combining various TEM methods (such as HR-TEM/STEM, electron diffraction, analytical EELS, EDX, quantitative ADF and discrete tomography) we were able to fully determine the chemical composition and the precise three-dimensional atomic configuration that is built from a bilayer of edge sharing (SiO$_4$)$_2$$^-$ tetrahedra. Furthermore, we observed both crystalline and vitreous regions of the silica that strikingly resembled Zachariasen's cartoons of a 2D network forming glass from 1932. For the first time the amount of structural order can directly be quantified by extracting radial distribution functions and ring-statistics from the atomically resolved micrographs (5.3.3). RDFs can be obtained from diffraction experiments as well. Ring statistics, however, are difficult, if not impossible, to measure directly in 3D glasses. These two standard metrics of structural models in glasses provide a quantitative measure of short, medium, and long-range order in our 2D silica and allow comparison to theoretical models for 2D and 3D glasses.

Furthermore, we found striking similarities between defects in 2D SiO$_2$ and the ones found in single-layer CVD graphene. Moreover, during continuous HRTEM imaging, we observed Stone-Wales transformations that are the most fundamental step in plastic deformations and for the transition from the vitreous to the crystalline phase (5.3.5). From this we can speculate to go far beyond simple structural investigations in the future and ask questions on the dynamics of these systems e.g. if the observed transformations can be understood within a rigid unit model.

All the above mentioned studies are of fundamental interest for material science and we are not aware of any other experimental setup (besides 2D materials in the TEM) that allows to address these questions on atomic scale and at a time resolution of approximately one second (future detectors will offer much better time resolution). This opens the possibility to cross-check and expand existing models. Fundamental new scientific insights, that are of general validity also for bulk materials, are gained especially from refinements of existing models, such as the broadening of the sputtering cross-section (3.1.1), the inclusion of chemical bonding into HRTEM image simulation (2.1.2) or the disagreement between experimental and simulated ring-statistics in vitreous silica (5.3.3, appendix A9).

Another interesting aspect of studying 2D materials in transmission arises from the extraordinary low specimen thickness and corresponding low contrast that gives experimental
access to the two surfaces. By this, graphene becomes the ideal substrate for HRTEM studies of adsorbates, e.g. small molecules (such as the perchlorocoronene molecule discussed in section 6.3) or thin films like 2D silica that may not be mechanically stable enough to be prepared free-standing. For the latter, we found that the 2D silica is energetically favored compared to the 3D phase only by van der Waals bonding to graphene. As a consequence, this material is formed and may only exist on the surface of another crystal such as graphene or Ru.

On the one hand, the possibility to do surface science within the TEM shows enormous potential already for pristine graphene: In chapter 3 we showed that e-beam damage can be studied in detail and the total damage could be separated into contributions of knock-on and chemical etching by the different voltage dependence. We propose to study the observed damage mechanisms in much more detail in 2D hetero-structures as demonstrated for a single layer of MoS\(_2\) sandwiched between two graphene layers in section 6.2. Therein the graphene layers acts as impermeable membranes and, as the interfaces between the layers are atomically flat, the MoS\(_2\) layer is in a very controlled carbon environment instead of an undefined HV atmosphere. On the other hand, combinations of different coatings, such as single-layer MoS\(_2\) sandwiched between two monolayers of h-BN offer the unique opportunity to gain very detailed insights into the underlying mechanisms and allows to separate the total damage into contributions from knock-on, pyrolysis and chemical damage. Moreover this new approach in sample preparation can serve to minimize or even completely avoid radiation damage as was the case for MoS\(_2\). This opens the door to atomic resolution imaging of beam-sensitive biological objects as outlined in chapter 6.
Bibliography


Bibliography


Appendix

List of Publications


List of Conference contributions


[C9] S. Kurasch Beam damage in graphitic materials SALVE Workshop 2011, Kleinwalsertal, Austria, (talk)


List of Conference contributions


List of Conference contributions

S. Eyhusen, G. Benner, and H. Rose Transmission Electron Microscopy at 20 and 80 keV for Imaging and Spectroscopy - Current Status and Future Prospects MC 2012, Kiel


Appendix 1

Experimental analysis of charge redistribution due to chemical bonding by high-resolution transmission electron microscopy

Experimental analysis of charge redistribution due to chemical bonding by high-resolution transmission electron microscopy

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The electronic charge density distribution or the electrostatic atomic potential of a solid or molecule contains information not only on the atomic structure, but also on the electronic properties, such as the nature of the chemical bonds or the degree of ionization of atoms. However, the redistribution of charge due to chemical bonding is small compared with the total charge density, and therefore difficult to measure. Here, we demonstrate an experimental analysis of charge redistribution due to chemical bonding by means of high-resolution transmission electron microscopy (HRTEM). We analyse charge transfer on the single-atom level for nitrogen-substitution point defects in graphene, and confirm the ionicity of single-layer hexagonal boron nitride. Our combination of HRTEM experiments and first-principles electronic structure calculations opens a new way to investigate electronic configurations of point defects, other non-periodic arrangements or nanoscale objects that cannot be studied by an electron or X-ray diffraction analysis.

The redistribution of charge that occurs when free atoms are arranged into a solid or molecule is of tremendous interest. It is the distribution of the binding electrons and their energy levels that defines, to a large extent, the properties of a material. According to the Hohenberg–Kohn theorem1,2, all ground-state electronic properties can be derived from the electronic charge density distribution; this theorem is also the basis for the density functional theory (DFT) approach to first-principles electronic structure calculations. The interatomic electrostatic potential is directly related to the charge distribution through Poisson’s equation, and hence, provides equivalent information. Charge density or electrostatic potential can be directly probed by the scattering of X-rays or electrons, respectively. However, a high precision is needed to obtain information that goes beyond the structure of the compound, so far obtained only from X-ray10 or electron diffraction11–13 experiments. Measurements of electronic charge densities can be used to reveal the nature of chemical bonds1 and to determine the ionicity of atoms in a compound14. Moreover, high-precision experimental data can be used to verify a calculated charge density15, even if a complete reconstruction is not possible16. This is particularly important for complex materials where the modelling, the involved approximations and discretization are not straightforward. For example, important details in the electronic configuration of copper oxide17 or magnesium diboride18 have been clarified by the combination of an electron and X-ray diffraction analysis with first-principles calculations.

In spite of these direct methods, most of our knowledge on crystal bonding and electronic structure comes from indirect evidence and theory19. One reason is the experimental difficulty to obtain charge density or crystal potential measurements with a sufficiently high accuracy. Moreover, diffraction experiments are limited to sufficiently large periodic structures, and hence, exclude the study of individual interfaces or point defects. In addition, there exist competing spectroscopic techniques that can provide information about the local electronic structure with high spatial resolution11–17. For example, atom-resolved electron energy-loss spectroscopy provides not only information about the elemental composition, but also adjustments to the energy levels from the local environment12–15. As another example, the combination of scanning tunnelling microscopy and spectroscopy can provide electronic spectra from interfaces or point defects18–20, but is inherently limited to surfaces.

Here, we show that a charge transfer between neighbouring atoms can be analysed on the basis of atomically resolved HRTEM. The effect of binding electrons on HRTEM image contrast has been explored through calculations in previous studies21–24, but the effects were not detected experimentally. However, in the same way as in X-ray or electron diffraction experiments, the influence of chemical bonds on HRTEM image contrast becomes discernible and relevant once a sufficient accuracy is obtained in the experiment. We demonstrate this for two cases that would both be inaccessible with a diffraction analysis. As a first example, we analyse the electronic configuration around nitrogen-substitution

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Figure 1 | Charge distribution, projected potentials and TEM simulations for nitrogen doped graphene. a. Relaxed atomic configuration for a nitrogen substitution in graphene. Bond lengths are given in angstroms. b. Projected potential based on the IAM, with the periodic components of the graphene lattice removed, and bandwidth limited to our experimental resolution (about 1.8 Å). Dark contrast corresponds to higher projected potential values, in accordance with our TEM imaging conditions. c. TEM simulation based on the IAM potential, for two experimental conditions (f1 and f2, see text). Filters are: (i) unfiltered, (ii) periodic components removed by a Fourier filter, and (iii) low pass filtered. d. Atomic structure (same bond lengths), with the changes in projected electron density due to bonding shown in colour. Blue corresponds to a lower, red to a higher electron density in the DFT result as compared with the neutral atom (IAM) case. e. Projected potential, filtered as in b. based on the all electron DFT calculation. f. TEM simulations using the DFT based potentials. The greyscale calibration bar applies to columns (ii) and (iii), which are all shown on the same greyscale range for direct comparison. The scale bars are 5 Å.

point defects in graphene. In this case, we demonstrate that the electronic configuration on the carbon atom next to the nitrogen is perturbed by the defect. In other words, electron scattering on the carbon atom next to the nitrogen is significantly different from electron scattering on a carbon atom elsewhere in the graphene sheet. The second example, hexagonal boron nitride (hBN), is well known to be ionic in the bulk form. We confirm the ionicity for the single-layer hBN structure from HRTEM measurements. Although single-layer hBN is crystalline, experimentally obtained free-standing single-layer hBN samples for HRTEM studies are only a few nanometres in size, and therefore a diffraction analysis is not practically possible so far. In both cases, the precisely defined sample geometries in terms of thickness (one layer), amorphous adsorbates and defects (none in the selected regions), along with very high sample stability and therefore unprecedented signal-to-noise ratios (by using lower acceleration voltages to avoid sample damage) enable sufficiently accurate measurements. Our analysis on the basis of HRTEM measurements provides a sensitivity to charge transfer on a single-atom level. This opens a new way to study electronic configurations, in particular for point defects, other non-periodic arrangements or nanoscale objects that cannot be analysed in a diffraction experiment.

HRTEM images are conventionally analysed on the basis of the so-called independent atom model (IAM), sometimes also called the procrystal model. In this model, the potential of a solid is calculated as a superposition of atomic potentials that have once been calculated for an isolated atom of every element. This is reasonable as a first approximation because the adjustments to the potentials due to bonding electrons are small. Moreover, the IAM result is useful for comparison, because the effects of chemical bonds can be easily recognized from the difference between the ‘real’ situation and the IAM approximation. Therefore, we will discuss the image simulations based on the IAM, as well as image simulation based on more accurate potentials from DFT calculations in comparison. Both, HRTEM experiments and first-principles electronic structure calculations, show that the IAM is not sufficient for accurate transmission electron microscopy (TEM) image simulations of our example materials.

We begin our results and discussion with the case of nitrogen-doped graphene. The atomic configuration has been considered in many previous works (for example, refs 35,36), and it was found that the C–N bond length in this configuration is nearly identical to the C–C bond length in graphene (with differences less than 0.1% (Fig. 1c). Then, on the basis of neutral, isolated-atom (IAM) scattering factors, one would not expect that a nitrogen substitution in graphene can be detected at all. The projected potential is almost identical to that of regular graphene (Fig. 1b), and the expected contrast difference between ‘neutral’ C and N atoms in the HRTEM simulation is less than 0.1% (Fig. 1c). The situation is different if we include the charge redistribution due to chemical bonds for this configuration. Figure 1d shows a model of the N substitution in graphene along with the changes in the electronic charge density due to the chemical bonds. As discussed above, we highlight these changes by showing the difference between the DFT and IAM result. In addition, we have removed the periodic components of the graphene lattice from this difference image (see Supplementary Information for the unfiltered images). Remarkably, the strongest change in the charge density is around the three carbon atoms next to the nitrogen substitution, rather than on the N atom itself. The reduced electron charge density around the nitrogen atom leads to a reduced screening of the core potentials, and to a spatially extended signal in the projected potential. The corresponding DFT-based projected potential (with periodic components removed, and bandwidth-limited to approximately our experimental resolution (about 1.8 Å)) is shown in Fig. 1e; here, we see a spatially extended dark contrast, with a diameter of approximately two times the C–N bond (red dashed circle in Fig. 1e). We emphasize that the
Experimental analysis of charge redistribution due to chemical bonding

Figure 2 | Nitrogen dopants in graphene. Imaging conditions and filters in a–f are the same as in Fig. 1c,f. The red lines in the CTF plots (insets in a,d,h) indicate the 2.13 Å graphene lattice spacing. a, c. Scherzer defocus images. The dark contrast can be directly interpreted as atomic structure. However, the nitrogen substitution defects are not significantly above the noise (red circles). d, f. Larger defocus images (f2) of the same area as shown in a, c. The nitrogen defects are clearly detected as a smooth dark contrast (in any case, a filter (e,f) is needed to discern the N dopants against the much stronger signal of the single layer graphene lattice). The extended defect (red dashed line in a) allows us to compare the same atomic position in both focus values. g, Image from a larger area, showing six nitrogen substitution defects marked by red arrows. The inset shows an unfiltered section of the image on the same contrast scale. h, Image of two nitrogen substitutions obtained with a reversed CTF (negative spherical aberration –Cs, positive defocus –f2), showing the substitution positions as white areas. i, Irradiation induced nitrogen substitutions (arrows, see text). The strong feature on the upper left is a beam induced hole. All scale bars are 1 nm.
signal due to bonding electrons here is not a point feature, as would be expected for a localized charge, an ad-atom or a heavier substitution atom. Hence, we can confirm from the experiment a charge redistribution over the nearest-neighbour atoms of a substitutional impurity, as shown below.

Indeed, the mostly lower-frequency components in the projected potential of the nitrogen substitution defect provide an additional complication to aberration-corrected HRTEM imaging of this defect. If we tune the spherical aberration and defocus so as to obtain a single pass-band in the contrast transfer function (CTF), the microscope acts as a high-pass filter and the defect is difficult to detect (about 0.3% contrast in a narrow point). This case is shown as ‘defocus f\textsubscript{2}’ in our images. Under these conditions, dark contrast can be directly interpreted in terms of the atomic structure; however, the nitrogen substitution cannot be distinguished from the carbon atoms (even at our very low noise levels). Using a larger defocus (f\textsubscript{1}), the CTF (Fig. 1c,f) shows oscillations but includes more of the lower spatial frequencies. Now, the nitrogen defect can be detected, yielding a stronger (about 0.6%) and also wider dark contrast. In any case, the nitrogen positions are most clearly visible when the graphene lattice is removed by a Fourier filter, or suppressed by a Gaussian low-pass filter. It must be emphasized that these filters are used only to detect and highlight the nitrogen defects in the experimental data, as otherwise the small perturbation to the regular graphene lattice is difficult to see by eye. The comparison between simulation and experiment, which provides the direct experimental verification of the DFT-based charge densities, does not require any filters (Fig. 3a, discussed further below).

Experimentally, we identify single-layer graphene areas in the nitrogen-doped, chemical vapour deposition (CVD)-grown graphene sheets by electron diffraction analysis\textsuperscript{27,28}. We record long image sequences, > 30 exposures with a pixel size of 0.2\text{\AA} and about 10\textsuperscript{6} counts per pixel, for each value of defocus. Importantly, the distance structure and defects of interest remain stable throughout the long exposure and associated high dose, which is a prerequisite to obtain the very high signal-to-noise ratio. Then, a drift-compensated average of 30–40 exposures is used. As predicted by the DFT model, the nitrogen substitutions exhibit a weak dark contrast in the larger defocus (f\textsubscript{2}) images, but disappear below the noise as the focus is set to the Scherzer defocus conditions (f\textsubscript{1}). As described above, this focus dependence confirms the mostly lower-frequency contribution in the projected potential for this defect.

Figure 2g–i shows additional images of N-doped graphene, with Fig. 2g being a larger area view of a CVD-grown sample. Figure 2h shows two nitrogen substitutions imaged with reversed contrast transfer (negative C\textsubscript{1}, positive defocus f\textsubscript{1}), where the substitution atoms are revealed as weak white spots. Figure 2i shows an alternative way to fabricate atomic substitutions in graphene: here, an undoped graphene sample was briefly exposed to higher energy electrons (300\text{\text{keV}}, about 10\textsuperscript{9} e\textsuperscript{−} nm\textsuperscript{−2}) and subsequently imaged at 80\text{\text{keV}} to prevent further damage. After such a treatment, we also find nitrogen substitution defects. A likely mechanism is a substitution of beam-generated vacancies by nitrogen atoms from the environment. However, we note that also a variety of other defects are generated by this approach.

A quantitative comparison between the simulation and experiment is shown in Fig. 3. For this comparison, the modulation transfer function of the CCD (charge-coupled device) camera was measured and applied to the simulated images, following the procedure of ref. 39. In addition, a small (0.7\text{\text{\AA}} full-width at half-maximum) Gaussian blur was applied to both, unfiltered experimental data and simulation, to reduce the pixel noise in the highly oversampled experimental data. As can be seen in Fig. 3a, an excellent confirmation of the DFT-based defocus conditions f\textsubscript{1} is obtained. Hence, our experiment confirms the DFT-based charge density and the corresponding electrostatic potential, whereas the IAM clearly disagrees with the experimental data.

We now turn to the calculations and measurements for the single-layer h\textsubscript{BN}. The conventional IAM TEM simulation is shown in Fig. 4a,b, and Fig. 4c,d shows the TEM image simulation for the DFT-based electrostatic potentials for the bonded configuration. In this partially ionic compound, charge is accumulated on the nitrogen site\textsuperscript{44}. Hence, we would expect a stronger screening of the N core potential, and thus a reduced contrast for this element. Nevertheless, the quantitative simulation result from the DFT calculation (Fig. 4e) shows a peculiar coincidence; the charge transfer happens to be such that the contrast difference between the B and N site, as expected from the neutral-atom (IAM) simulation, is almost exactly cancelled. In other words, single-layer h\textsubscript{BN} looks identical to graphene in HRTEM images (at our conditions) because of its ionic character. Thus, we can confirm the DFT prediction and verify the ionicity of single-layer h\textsubscript{BN} from HRTEM images, but we cannot assign the B and N sublattices.

For the experimental case, the separation of intrinsic contrast (that is, that of the sample) and effects of optical aberrations (from the microscope) is very important, and discussed in more detail in the Supplementary Information. The effects can be separated by the comparison between single-layer and bilayer h\textsubscript{BN}. For a bilayer, a symmetric profile is expected owing to the symmetry of the projected structure (B is above N). Hence, any asymmetry in the bilayer profile represents only the residual electron optical aberrations. Assuming identical imaging conditions for all points of the sample, the comparison between a single-layer and bilayer region would show the ‘intrinsic’ contrast difference in the monolayer, if present (however, the assumption of identical imaging conditions in separated areas is not always justified—

### Notes

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**Figure 3** | Analysis of the nitrogen substitution defect. a. Comparison between experiment and simulations based on IAM and DFT potentials for defocus value f\textsubscript{1}. MTF: modulation transfer function. Inset: The image and profile, and the Fourier filtered image (graphene lattice removed). The noise level is measured as the standard deviation in a featureless region of the filtered image, close to the defect (black rectangle). A standard deviation of 0.0008\text{\text{\AA}} is found in this example. b. Line profile with the periodic components removed. The intensity dip at the nitrogen defect is seven times stronger than the standard deviation, and thus clearly above the noise.
Experimental analysis of charge redistribution due to chemical bonding

Figure 4 | Simulated TEM images for hBN. a, b. Conventional, IAM TEM image simulation for single layer hBN. c, d. TEM simulation using potentials from the all electron DFT simulation. e. Intensity profile plots for the two simulations. The scale bar in d is 1 Å.

Figure 5 | Experimental data for hBN. a. Image of single and bi layer hBN (scale bar is 5 Å). The unit cells indicated by the red dots were chosen for analysis (away from defects and edges); shown here is the average and standard deviation. b. Intensity profiles from the single and double layer average (standard deviation as error bars). The contrast of the double layer was numerically reduced by a factor of 2 for comparison. The intensity minimum on the left sublattice shifted to the same value (pink line), and then the intensity on the right sublattice is compared (blue lines). The contrast difference expected from IAM and DFT model is indicated.

As we have shown, details of the electronic configuration can be detected in TEM images with a high signal-to-noise ratio obtained under carefully controlled conditions. One key ingredient is the fabrication of samples with precisely defined geometries, and a reduction of radiation damage to allow sufficiently high signal-to-noise ratios. Graphene and hBN are special because they are easy to prepare in such well-defined geometries, and maintain their crystalline surface configurations even under ambient conditions. On this basis, we can speculate what would be required to detect charge transfer in other systems. We note that much larger chemical shifts than detected here have been predicted for a variety of materials in refs 23,24, but could not be measured owing to artefacts of common TEM sample preparation methods. The obvious implication is that one would need new ways of sample preparation and transfer to the TEM, because the surfaces of many materials become amorphous already by exposure to ambient conditions. Moreover, the low-voltage electron beam seems to be important to avoid sample amorphization (including the sample surface) in the electron beam. The single-layer thickness of the sample, however, is most likely not a key requirement, as can be deduced from the earlier calculations.23-24

In our examples, the experiments confirm the DFT-based potentials (and thereby the charge densities), which might not be too surprising given that these are relatively simple systems. Nevertheless, we successfully distinguish between two candidate
models for the charge distribution (IAM versus DFT) that differ only in the distribution of binding electrons. This is achieved for a non-periodic configuration, a single-atom point defect. It is therefore straightforward to see the potential case, where a charge distribution for a micromagnetic configuration is not so easy to model, and then a HRTEM experiment may provide important guidance. We have demonstrated the case of a point defect, and calculations in ref. 22 indicate that charge transfer at an interface may also have similarly detectable effects. Finally, we note that electron holography experiments should in principle provide the same information as we show and discuss here, that is, information that is contained in the projected potentials.

At the same time our results also show that, in cases where small differences in elemental contrast are important, bonding effects have to be taken into account. For example, the contrast difference between the B and N sublattices in HfBN images of hBN single layers is much smaller than expected from the IAM approximation, and the experiment confirms this prediction once the imaging conditions are suitably controlled. Hence the question of which elements forms the stable mono-vacancies in hBN surfaces under TEM observation remains unclear. For the case of N-doped graphene, one would expect from IAM simulations that a N substitution in graphene cannot be detected. It is exclusively the effect of binding electrons that makes it possible to find nitrogen substitutions in graphene. Nitrogen substitutions in graphene—possibly irradiation-induced—also provide an alternative explanation to the weak dark contrast observed in ref. 40 (nitrogen substitutions had been ruled out on the basis of IAM calculations with atomic configurations from the literature, whereas a DFT-based calculation provides a reasonable agreement).

As another remarkable point, the contrast of the N defect is primarily due to a change in the electronic configuration on the neighbouring carbons, rather than on the nitrogen atom itself, and it is due to a little dipole in the charge density on these atoms. Hence, it is also not possible to model these effects by using modified scattering factors for partly ionized atoms.

We have shown that it is possible to obtain insights into the charge distribution in nanoscale samples and non-periodic defects from HRTEM measurements. For our examples of the nitrogen substitutions in graphene and hBN layers, we can assign experimentally observed contrast features to details in the simulated electron distribution. We can detect a single light substitution atom in graphene, which is possible only because of the electronic effect. In the case of hBN, the charge redistribution leads to a loss of the elemental contrast difference. Instead, the ionic character of the interface is established. We can detect a single light substitution atom in hBN, and the experiment confirms this prediction once the imaging conditions are suitably controlled.

References

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Author contributions


Additional information

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EXPERIMENTAL ANALYSIS OF CHARGE REDISTRIBUTION DUE TO CHEMICAL BONDING BY HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

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SUPPLEMENTARY INFORMATION

I. SYNTHESIS OF N DOPED GRAPHENE

Nitrogen doped graphene is prepared by Chemical Vapor Deposition (CVD) with nickel (Ni) or copper (Cu) as a catalyst. It mostly follows the procedure which has been developed for pristine graphene and results in high quality graphene [1, 2] and graphene membranes [3], with the addition of ammonia as nitrogen source during part of the synthesis [4]. The experimental procedure for nitrogen doped graphene growth using both catalysts is same except reaction time (3 min for Ni and 20 min for Cu).

In detail, a Ni or Cu film with 300 nm of thickness was coated onto a SiO₂/Si substrate using an electron beam evaporator. The metal coated substrate was located on the middle of a quartz tube and heated to 1000 °C at a 40 °C/min heating rate, under a flow of argon (500 sccm) and hydrogen (500 sccm). The metal film on SiO₂/Si was annealed further at 1000 °C for 20 min. A mixture of gases with a composition (CH₄ : Ar : H₂ = 200:500:2500 sccm) was introduced at 980 °C for 3 min (Ni) or 20 min (Cu). Then, the sample was cooled down at a rate of ca. 6.7 °C/min. During cooling, ammonia was introduced instead of CH₄ within the temperature range of 800 °C to 400 °C (introducing ammonia at higher temperatures destroyed the metal layers). The sample is then further cooled down to room temperature under Ar (200 sccm) and H₂ (500 sccm) flow. For transferring the doped graphene layers onto a TEM grid, poly(bisphenol A carbonate) (PC) was dissolved in chloroform (solid content: ~15 wt%). The PC/chloroform solution was spin-coated onto the graphene/metal/SiO₂/Si substrate with 500 rpm for 2 min. The PC was deposited onto the substrate homogeneously with ~10 µm of thickness. The graphene/PC film was released freestanding by chemical etching of the Ni layer with a FeCl₃ (1 M) solution. The etching time varied depending on the substrate size from 30 min to 12 h. The etching was followed by immersion in a concentrated HCl solution (12 h) in order to remove amorphous carbon residue. The graphene/PC film was rinsed several times with DI-water and dried with nitrogen gas. It was then placed onto the TEM grid, and the PC was dissolved using chloroform. Before inserting into the microscope, in order to further reduce adsorbed contamination, the TEM grid with graphene layer was heated in air to 200 °C for 10 minutes.

The presence of nitrogen in the doped samples was verified by Auger spectroscopy (Fig. 1). A small signal at the N KLL energy is found (enlarged as inset in Fig. 1), which is not present in undoped reference samples. The other lines in the spectra correspond to carbon, oxygen (presumably physisorbed after air exposure) and copper, and are also found in the undoped graphene...
Figure 1: Auger spectrum showing the existence of nitrogen in a graphene sheet, grown on a Cu substrate by the CVD method with the addition of ammonia.

reference samples. Auger spectroscopy was performed using a JEOL JAMP-7810 scanning Auger microprobe at 15keV.

II. ADDITIONAL IMAGES FOR N DOPED GRAPHENE

Fig. 2a shows the DFT relaxed configuration of N doped graphene as used in all simulations. Fig. 2b-d shows some additional observations from nitrogen doped graphene. Fig. 2b shows an example of an unexpected defect configuration that was frequently found in the nitrogen doped samples that were synthesized on the Ni surface. It consists of seven hexagons that are rotated by 30°, connected to the graphene lattice by six pentagons and heptagons. Due to its peculiar appearance we will refer to it as flower defect. Its formation mechanism remains unclear at this time. Remarkably, the flower defect is not a reconstructed vacancy; i.e., it contains the same number of atoms as the ideal graphene sheet.

We note that the nitrogen defect is reactive [5], at least in comparison to the inert carbon surface. Frequently, the nitrogen substitution defects have isolated ad-atoms trapped on top at the beginning of the observation, which then detach under electron irradiation after a few exposures and then reveal the isolated nitrogen substitution defects. These ad-atoms are trapped on the nitrogen atom or its neighbouring carbons. In some cases, we observe a repeated trapping and de-trapping of contamination atoms on the nitrogen defect in long image sequences. The sequence in Fig. 2c is
Figure 2: Nitrogen doped graphene. (a) DFT relaxed configuration of a single nitrogen substitution in graphene, with bond lengths given in Å. (b) Single-layer graphene membrane with the flower defect. Inset shows a structural model. (c,d) Sequences showing repeated trapping and detachment of contamination atoms on the nitrogen substitutions. Sequence (c) is recorded at Scherzer defocus (ca. 10nm) and (d) at an underfocus of ca. 18nm, with the lattice contrast removed by a Fourier filter. All scale bars are 1 nm.

recorded at Scherzer defocus and shows direct structure images. An ad-atom is present initially, desorbs in intermediate images, and another ad-atom is again trapped in the same place (within one nearest neighbour). Sequence (d) is recorded at the larger defocus (-18nm, optimized for N substitution detection), the lattice is filtered out. Here, several events are observed where an ad-atom is trapped on the same position. Indeed, this dynamics provides an independent confirmation of the nitrogen defect in this position: The repeated trapping of ad-atoms in the same position (within one nearest neighbour) proves that there must be some kind of reactive defect within
the single layer graphene sheet at this point. However, the intermediate frames appear identical to undisturbed graphene within the noise level of single exposures, which allows only substitutions of similar atomic number (B, N, O) as alternatives to carbon. Then, given the intentional presence of nitrogen during synthesis of these samples, we can identify these defects as nitrogen substitutions. For the nitrogen substitution analysis as shown in the main article, we have to use averages from several exposures. For this purpose, we only use parts of the image sequences where no ad-atom is visible in all individual exposures.

In Fig. 3 we show further TEM images of nitrogen substitutions in graphene. Fig. 3a,b shows the comparison of a nitrogen doped sample and an un-doped reference graphene sample. In this case, Fig. 3a shows a graphene sheet grown on a Ni surface in presence of ammonia, and Fig. 3b shows a graphene sample that was prepared by mechanical cleavage [6] (and not irradiated above the knock-on threshold [7]). Fig. 3c,d shows a sample that was also prepared by mechanical cleavage, briefly irradiated with 300keV electrons (with a dose of ca. 10^7 e⁻ nm²). The sample shown in Fig. 2i of the main article was left in the microscope vacuum between irradiation and imaging (ca. 2 hours later), while the sample in Fig. 3c,d was exposed to air. In both cases, we observe nitrogen substitution defects. A likely mechanism is a substitution of irradiation-induced vacancies by nitrogen atoms from the air or from residual gas in the vacuum. Indeed, the sequence in Fig. 3c,d shows one example where a vacancy defect converts into a nitrogen substitution defect during observation. All images in Fig. 3 are averages of ca. 40 exposures, recorded at a defocus of f₂ ≈ −18nm and a gaussian low-pass filter was applied such that the graphene lattice is almost suppressed but still discernible. Also, we note in the larger-area views (Fig. 3a,b) that the imaging conditions are close to ideal only near the amorphous adsorbates that are used for fine tuning. The contrast of the nitrogen substitution is only weakly dependent on small residual non-round aberrations. Therefore, this topic is discussed in more detail below in the context of hexagonal boron nitride images, where it is important for the analysis.

III. DETAILS OF THE VASP DFT SIMULATION

Spin-polarized DFT calculations were carried out with the Vienna ab initio simulation package (VASP) [8]. The structure of the substitution defects in graphene was relaxed using the exchange-correlation functional by Perdew, Burke and Ernzerhof (PBE) [9]. Ionic cores were represented by the projector augmented-wave (PAW) method [10, 11]. An energy-cutoff of 400 eV was used...
Figure 3: Further images of nitrogen substitutions in graphene. (a,b) Comparison of a nitrogen doped sample (a), and an un-doped graphene sample (b). 9 nitrogen substitutions are visible as weak dark spots and indicated by red arrows in (a). The heavy dark spot (red dashed circle) is most likely an ad-atom trapped on a nitrogen defect (see Fig. 2c,d). (c,d) Irradiation-induced nitrogen substitutions in two subsequent images. In one case, the transition from a vacancy-type defect to a nitrogen substitution is observed. All scale bars are 1nm.

For the calculations. With these parameters, the pure graphene layer has a relaxed C-C-distance of 1.424 Å. For the calculations of the defect structure, a 4x4 supercell of the hexagonal graphene unit cell was used (lattice constant: 9.868 Å). We employed a large 9x9x1 k-point mesh with a Gaussian smearing of 0.1 eV for the k-point summation in order to ensure well-converged geometries of the considered structures. Different initial configurations with the nitrogen atom slightly displaced in different directions all resulted in the same relaxed structure. The relaxation process was stopped...
when all forces were smaller than 0.002 eV Å⁻¹.

IV. DETAILS OF WIEN2K DFT SIMULATION

The all-electron WIEN2K DFT simulation is used to obtain the electron charge density and electrostatic potential, for a structure with fixed atomic coordinates. For boron nitride we use the literature value of \( a = 2.505 \text{ Å} \) [12] (separation between B and N atoms of \( a_{BN} = 1.45 \text{ Å} \)), and for nitrogen doped graphene we use the relaxed configuration described above (see Fig. 2a). We have evaluated the required number of k-points and size of the base set (RKMAX) by convergence tests. To this end, we have not only tested a convergence of the total energy and electric field gradient, but also of our value of interest, the projected potential values. For the results shown in the main article, we used 54 k-points with 15x15x3 division for the hBN results. For the nitrogen substituted graphene supercell, we used 8 k-points with 4x4x1 division and RKMAX=8. The muffin-tin radius is set automatically by WIEN2K to create spheres that touch with the nearest neighbours. All other values are left to the defaults of the WIEN2K software (version 9.1).

V. IMAGE SIMULATION BASED ON WIEN2K RESULTS

A. Overview

For the TEM image simulation, it is important that all electrons are included in the simulation, and not only valence electrons. For this reason, we extract the electrostatic potentials from the WIEN2K results. This software was also used by Deng and Marks in Ref. [13]. However, they used X-ray scattering factors calculated by WIEN2K and transformed them to electron scattering factors using a modified version of the Mott-Bethe formula [14], while we extract potentials directly from WIEN2K. The advantage of our approach is the simplicity and in principle the possibility to carry out multi-slice simulations (not needed for our samples), while the drawback is a very fine required sampling of the potential and associated high computing time. The WIEN2K software calculates the electrostatic potential created by all electrons and all core charges. This potential is stored in a file called case.vcoul and contains the Coulomb potential in a lattice harmonics representation and as Fourier coefficients. The utility program lapw5 can be used to obtain linescans and 2d slices of this potential file. A large number of 2d slices is then extracted to ob-
tain the 3d potential. We then calculate the projected potential in the direction of view of the TEM (i.e., normal to the graphene or hBN layers), and simulate the effect of the microscope as described further below.

**B. Electrostatic potentials**

The aim of the next section is to clarify that the potential extracted from WIEN2K can be used directly for TEM image simulation. As a first test, we compare the results for an isolated atom with existing isolated-atom potentials. In Fig. 4 we see the comparison between the WIEN2K starting potential and two different isolated atom potentials by Doyle and Turner [15] and Kirkland [16]. The WIEN2K potential was obtained by defining a rectangular unit cell of $10 \times 10 \times 10\text{Å}$ with a single carbon atom inside. The starting charge density and the corresponding potential files were calculated and a linescan with a resolution of 250ppÅ was created using the utility program lapw5. Far from the core the WIEN2K potential becomes constant but not zero. The linescans were shifted in z-direction (until the smallest value was equal zero) to obtain the WIEN2K potential in the common normalization. One factor that complicates this normalization is the fact that the WIEN2K potential starts to oscillate in the vacuum region, which is probably caused by the limited size of basis functions. However, the oscillations and deviations occur only in vacuum regions where the potential is very small and therefore do not affect our results. From the graphs in Fig. 4, we see that the WIEN2K and Kirkland potential agree very well in the core region where, in contrast to the Doyle Turner potential, both of them are divergent.

The excellent agreement of the isolated-atom potential from WIEN2K to the Kirkland potentials shows that the WIEN2K potentials are well suited for TEM simulation, and small changes from bonding should not affect this point. As a further useful fact, we found that the starting potentials from WIEN2K (i.e., results obtained with zero iterations of the DFT computation) are practically indistinguishable from the Kirkland potentials. In other words, the WIEN2K DFT simulation uses the independent-atom electron distribution as starting configuration. This provides an easy way to obtain an independent-atom (conventional) TEM simulation result for comparison with the DFT based result: Simulated images based on potentials extracted with zero iterations in WIEN2K correspond to the conventional (IAM) TEM simulation, while bonding effects are taken into account after the DFT based changes in the electronic configuration have been computed. In this way we can compare IAM and DFT results in a way that uses precisely the same algorithms.
Figure 4: Carbon atom electrostatic potentials, using the parametrization of Doyle and Turner [15], the parametrization of Kirkland [16], the electrostatic potential extracted from WIEN2K for an isolated atom, and the unscreened Coulomb potential of the nucleus for comparison in a linear and double logarithmic plot.

An important point that remains in working directly with the electrostatic potential in an equidistant 3-d grid is that we are making a discretization of a function that has poles at the positions of the nuclei. In this case, sampling points around the nucleus may not adequately represent the integrated potential of the corresponding volume element. In the extreme case, a sampling point may fall onto the position of the nucleus and thereby contribute an infinite value, multiplied with a finite volume element. To overcome this problem, we sample the electrostatic potential at a much higher spatial resolution than needed for image simulation, and use a global cut-off parameter for the potential to avoid infinite contributions. In other words, we mitigate the effect of the “bad pixel” at the position of the nucleus by using a very fine sampling, and subsequent averaging (this averaging or smoothing is inevitably part of the TEM simulation for the much lower realistic experimental resolution in the following step). Then, the main question is what sampling (points per Å) is needed, and how much error one has to expect as a result. To get an idea of the numbers, sampling at 30 points per Å and required (experimental) resolution of only \( \approx 1 \text{ Å} \) means that there are \( 30^3 = 27000 \) volume elements within a 1 Å cube, of which only one, which includes the nucleus, is affected by the cutoff. In this respect, it is important to note that the cut-off is implemented on the 3-D potential, and not the (2-D) projected potential which serves as input for the simulation.

The required number of points is determined in a convergence test, where we use the integrated
Figure 5: Integrated potential of a single carbon atom, extracted from the WIEN2K electrostatic potential using different numerical sampling and different cutoff values for the singularity at the nucleus. Also, the atom was placed halfway in-between sampling points (left) and onto a sampling point (right). At a sufficiently high sampling rate, all results converge to the same value.

The integrated potential of the atom as the figure of merit. This is reasonable since, at the rather low experimental resolution (compared to the sampling in the simulation), only the integral value from the core region of the atom is relevant. In Fig. 5, we show the integrated potential for an isolated atom after extracting the potential with different sampling and different cutoff values. Also, the nucleus was placed onto the sampling point and in-between for comparison. As cut-off method, we use a nearest-neighbor cutoff, meaning that the potential value is reduced to that of the nearest pixel if it exceeds 30000 or 50000 volts, and a fixed cutoff of 1590V (maximum of the Doyle-Turner potential for carbon). If we use no cut-off, one would expect an infinite value if the atom is on the sampling point (an infinite value multiplied with a finite volume element numerically) but the maximum output value from lapw5 is $1.6 \times 10^6 \text{V}$ (i.e., effectively another cutoff due to the numerical value range). Even with this extreme variation of values for the volume element that includes the nucleus, the integrated potential precisely arrives at $(119.8 \pm 0.1) \text{V} \cdot \text{Å}^3$ for the highest sampling. In other words, the value of this one volume element does not matter if simply a sufficiently high sampling is used. The value is also in a very good agreement with the integrated potential from the Doyle-Turner parameters [15] of $120.03 \text{V} \cdot \text{Å}^3$ (which can be integrated analytically). Further, we can conclude that a sampling of 25-35 ppÅ is sufficient for our purposes if we use a reasonable cut-off algorithm. For the results presented here, we use a sampling rate of 104 ppÅ (hBN) and 52 ppÅ (N doped graphene unit cell) with the 50 kV nearest-neighbour cutoff.
As a further cross-check, we note again that we can obtain both the conventional (IAM) and DFT-based TEM simulation from the starting and final electron distribution in WIEN2K. For both cases, we use precisely the same sampling, integration, and positions of the nuclei with respect to the sampling points. Effects from poor sampling of the potential close to the nucleus, if present, would occur in both cases with the same magnitude (the positions of the nuclei are the same, and the electron charge density does not contain singularities). Hence, any sampling effects would show up in the comparison of our IAM result to other IAM simulation codes, based e.g. on Doyle-Turner potentials (which avoid the singularity), and this is not the case.

C. TEM image simulation

The previous section described how to obtain accurate electrostatic potentials on the atomic scale for a given structure in a way that includes the effects of chemical bonding. The first part of a TEM image simulation is now to model the effect of the sample on the electron beam. Since our samples consist of a single atomic layer, we use a single projection of the electrostatic potential. Then, the effect of the sample is simply a phase shift in the electron wave which is proportional to the projected electrostatic potential

\[ \Psi(x, y) = \Psi_0(x, y) \ast \exp(-i\sigma V_z(x, y)) \]

where \(\Psi_0(x, y)\) and \(\Psi(x, y)\) is the wavefunction before and behind the sample, respectively,

\[ V_z(x, y) = \int V(x, y, z)dz \]

is the projected potential, and \(\sigma = \frac{2\pi m e \lambda}{\hbar^2}\) the interaction parameter (where both electron mass \(m\) and wavelength \(\lambda\) depend on the electron energy; \(e\) is the electron charge, \(h\) is the Planck constant). The projected potential is calculated numerically from the 3-D potential obtained from WIEN2K as described above.

The second part of the TEM image simulation is to model the effect of the microscope, which follows the standard approach as in Chapter 3 of Ref. [16]. We use a spherical aberration of 20\(\mu m\), an acceleration voltage of 80kV, a focal spread of 5nm, and a convergence angle of 0.5 mrad. The two defocus values are \(f_1 = -90\,\text{Å} \) (Scherzer defocus) and \(f_2 = -180\,\text{Å} \) (graphene lattice in the second extremum of the contrast transfer function (CTF)). The corresponding phase plates (including damping envelopes \(E(q_x, q_y)\)) are shown in Fig. 6a,b. Experimentally, imaging conditions
Figure 6: Contrast transfer at the conditions used in this work. (a,b) Phase plate $\sin(\chi(q_x, q_y))E(q_x, q_y)$, for focus $f_1$ and $f_2$ as used for the simulations. Blue and red represents positive and negative values, respectively. (c,d) Square modulus (logarithmic greyscale) of the phaseplates. Red dots in (a-d) indicate the 2.13Å (1 – 100) graphene reflections. (e,f) Power spectra (log scale) of the experimental images from a small amorphous adsorbate on the graphene sheet close to our region of interest.

can be verified from the thin amorphous adsorbates that cover some parts of the graphene sheet. Fig. 6e,f shows the Fourier transform from such adsorbates, recorded in the same images and only a few nm away from our features of interest. For focus value $f_1$, the single, continuous pass-band with the graphene lattice spacing at the outer rim is clearly visible in Fig. 6a,c,e. For focus value $f_2$, a single dark ring in the power spectrum, just inside the graphene lattice spacing, is expected and confirmed in the experimental data (Fig. 6b,d,f).

VI. TEM DATA ACQUISITION AND PROCESSING

TEM imaging was carried out using an image-side spherical-aberration corrected Titan 80-300, operated at 80 kV, with the exception of Fig. S3c,d (50 kV) and Fig. S13 (100 kV). The extraction voltage of the source was reduced from its standard value (ca. 4 kV) to 2 kV, in order to obtain a lower energy spread. Images were recorded on the CCD camera (1k x 1k, Gatan MSC 742) or
the CCD camera within the Gatan Imaging Filter (GIF), a 2k x 2k camera (Model US1000). The GIF camera was operated in a 2x binning mode in order to obtain a faster read-out; i.e. we were effectively using it as another 1k x 1k camera. In both cases, we use a sampling of 5 pixels per Angstrom (referring to the binned pixel size for the GIF camera).

Image sequences are recorded with ca. $10^4$ counts per pixel, 1 second exposure time, and ca. 2 second intervals. Effects of slightly uneven illumination are removed by normalization (division) to a copy of each image with a very large Gauss blur (> 40Å FWHM) applied. In this way, the long-range variations of the uneven illumination are removed, and at the same time the mean intensity is normalized to 1 throughout the image. The image data is upscaled to a 2x higher sampling (0.1Å pixel size) prior to image alignment, to avoid interpolation artefacts. Image registration is done with the Stackreg-plugin [17] for the ImageJ software, which provides sub-pixel accuracy for image alignment. In addition, Fig. 5a of the main article was rotated to be aligned with the crystal orientation. Fig. 7 shows the Fourier filters that were used on the experimental data in order to find and show the nitrogen substitution defects. Note that applying a gaussian blur in real space is mathematically equivalent to a Gauss-shaped low-pass filter on the Fourier transform. Low-pass filter #1 (Fig. 7c) corresponds to a 0.7Å FWHM Gauss blur, while Low-pass filter #2 corresponds to a 1.7Å FWHM Gauss blur.

VII. ADDITIONAL CALCULATION RESULTS FOR NITROGEN DOPED GRAPHENE

Although the TEM image depends directly on the electrostatic potentials, it is instructive to look at both, the projected potentials and the charge densities for IAM and DFT calculation. These two properties are related to each other via Poisson’s equation in the three-dimensional volume (however, note that we are showing the projected charge densities and potentials here). The difference between the IAM and DFT results shows how charges are re-arranged upon bond formation. Fig. 8a and b show a projection of the charge density, for the IAM and the DFT calculation, respectively. The change from a spherical charge distribution (IAM, Fig. 8a) to the charge distribution that is smeared out over the bonds (Fig. 8b) is apparent in the comparison of these two images. Fig. 8c shows the difference in the projected electron charge densities. In order to estimate a degree of ionization, it is necessary to define a volume surrounding each atom (i.e., an area in the projected charge density), and any choice here is of course arbitrary. First, we measure the excess charge on the nitrogen atom itself, by choosing a surface that cuts between the C and N
Figure 7: Fourier filters employed in this work. (a,b) Fourier transform (power spectra) from a graphene image, including amorphous adsorbates near the region of interest. (a) Unfiltered Fourier transform, (b) with Fourier filter to remove the periodic components of the graphene lattice applied and indicated by red circles. The filter was applied in Fig. 2b+c of the main article. (c) Low-pass filters, graphene lattice spacing is indicated by vertical black lines. Low-pass filter #1 is used to remove the high-frequency pixel noise, and does not significantly affect the experimentally available information (which extends only up to ca. 0.55 Å⁻¹). This filter was applied in Fig. 3a of the main article. Low-pass filter #2 is used to suppress the graphene lattice contrast, in order to find and highlight the nitrogen substitution defects in the experimental data. It was applied to Fig. 2c,f,g,h,i of the main article and Fig. 3 of the supplementary information.

atom (red circle in Fig. 8c). Here, the change is only +0.07e⁻ as compared to a neutral atom (in agreement with a previous calculation [5]). Remarkably, the nitrogen atom itself is almost neutral and in fact is charged with the wrong sign to explain a dark contrast. Also, all carbon atoms are nearly neutral when choosing such a cylindrical boundary around the atoms. However, a hexagon shaped boundary through the nearest carbons (yellow in Fig. 8c) shows a difference of −0.31e⁻ in this larger region (including the central circle). This reduced electron density, or positive net charge (reduced screening of the core potential) spread over a larger area, explains the smooth dark contrast associated to the nitrogen substitution. This charge is then mostly screened over a further atomic distance (blue hexagon). Further insight can be gained by removing the periodic components of this difference image, shown in Fig. 8d: From this image, it is clear that the most dominant effect is a dipole-shaped rearrangement of the electrons on the nearest-neighbour carbons around the nitrogen defect. Again, this delocalized charging effect agrees with the smooth appearance of the nitrogen defect in graphene as predominantly lower frequency components in the high-resolution experimental images.

A similar analysis is shown for the projected potentials in Fig. 8e-h. Here, the potential differences are given as relative differences (DFT-IAM)/DFT. In the comparison of the projected
Figure 8: Analysis of the nitrogen defect calculation results. (a-d) Analysis of the projected electron density, (a) IAM and (b) DFT result (log greyscale, white corresponds to a higher charge density). (c) Difference DFT-IAM, showing charge rearrangement due to bonding (linear greyscale, white corresponds to a higher charge density in the bonded configuration). Charge differences in the marked regions is given on the right hand side. (d) Charge density difference (DFT-IAM), with periodic components of the graphene removed. The dipole-shaped charge on the carbon atoms next to the nitrogen atoms is indicated in one example as orange-blue line. (e-h) Analysis of the projected potentials, (e) IAM and (f) DFT result (log greyscale). (g) Difference DFT-IAM (linear greyscale). Dark corresponds to high projected potential values. Relative differences listed on the right hand side are (DFT-IAM)/DFT. (h) Difference in projected potentials, with periodic components removed (mask used in d,h is shown as inset). Scale bar is 1 Å.

potentials, it should be noted that already for ideal graphene, the mean inner potential is reduced by 15% in the DFT result as compared to the IAM (this effect might be detectable e.g. by electron holography, which would be better suited to measure absolute potential values at low spatial frequencies). The important insight here is that we obtain an extended region around the nitrogen defect where the projected potential is higher than in the surrounding graphene, visible in Fig. 8g,h as extended dark area.

VIII. ADDITIONAL CALCULATION RESULTS FOR HEXAGONAL BORON NITRIDE

We analyze again both the projected potential and charge distribution, shown for hBN in Fig. 9. In the charge density, the change from a roundish (IAM, Fig. 9a) to a triangle-shaped distribution...
Figure 9: Projected electron charge densities and projected potentials for single layer h-BN for the IAM and our DFT simulation. White corresponds to a high electron density or high projected potential. (a,b,d,e) are represented on a logarithmic greyscale, while (c,f) use a linear greyscale. (a,b) projected electron charge density for IAM and DFT, respectively. The change from a roundish shape of the electron cloud (a) to a triangular shape (b) due to bonding effects is visible. (c) Differences (DFT - IAM) in the projected charge density, i.e., charge shifts due to bonding. Using the half-unit-cell boundary as indicated, a shift of 0.2 electrons from B to N is found. (d,e) projected potentials for IAM and DFT. In the DFT result (e), the core potentials are screened over a shorter distance, resulting in a “sharper” appearance of the atoms as compared to (d). Correspondingly, the mean inner potential of the whole unit cell is decreased by 14% in the DFT result. (f) Differences in the projected potential, integrated over the indicated areas. Relative differences are given as (DFT-IAM)/(IAM).

(DFT, Fig. 9b) is apparent in the comparison. Fig. 9c shows the difference in the projected electron charge densities. If we split the unit cell into two equal areas as indicated by the triangles in Fig. 9c, we find that 0.2 electrons shift from the boron to the nitrogen atom due to bonding (note that this value of partial ionization depends strongly on how these volumes are defined). In the projected potentials, we find that the mean inner potential (the volume average of the potential) is 14% lower in the DFT result as compared to IAM. In the DFT result, the core potentials are screened over a shorter distance than in IAM, resulting in a slight reduction of atomic contrast and a sharper appearance of the atoms. However, this effect is stronger on the N site, leading to a practically cancelled contrast difference between B and N at our experimental conditions. The accumulation of charge on the nitrogen site is in agreement with the analysis of h-BN in the literature [18]. Again, the experimental TEM data confirms this ionic character of h-BN for the single layer, and rules out the neutral atomic configuration.
Figure 10: Simulations from IAM and DFT for different resolution. Shown is the projected potential, bandwidth-limited by different apertures. Profile plots are normalized to the “hole” in the center of the hBN hexagon (value 0) and the nitrogen site (value -1). The light-blue area indicates as reference an experimental error of 5% contrast difference between the atomic sites.

Based on the accurate electrostatic potentials from the all-electron DFT calculation, we briefly discuss the requirements for identifying the B and N sublattices in hBN single layer TEM images. For simplicity we show here the projected electrostatic potentials, limited to a specific resolution by apertures as indicated. In the real experimental case, the effect of the microscope would have to be modeled on top of this by an additional Fourier filter. However, at a given spatial resolution there can not be more information in the final image, than is already present in the projected potentials.

The analysis is very simple if only the first Bragg reflection (1-100, corresponding to 2.16Å) is transferred. In general, the image of the hexagonal structure in this case is characterized by three values, the contrast on the three sub-lattices (B site, N site, hole in the hexagon). Further, the double-layer image can be used to verify the effects of residual aberrations. The IAM simulation with this aperture in Fig. 10 illustrates that it is in principle possible to have a different contrast for B and N sites at this resolution, even though the atomic separation is only 1.45Å. It has to be considered as a coincidence that the ionic character of the material leads to a practically symmetric contrast in the DFT based simulation. Importantly, our experiment confirms that no
distinction between B and N sites is possible at this resolution, even with very high signal to noise ratio.

The situation is not changed by including the \((2 - 1 - 10)\) reflection into the image. This reflection cannot carry any “which-atom” information already for symmetry reasons. It corresponds to a 1.45 Å spacing in a hexagonal structure that adds the same contributions to the B and N sites (the relative numbers in Fig. 10 are slightly different due to the chosen normalization).

Only after including the 1.08 Å (2-200) reflection, we expect a clear difference between B and N sites based on the DFT model. Also, the relative difference between IAM and DFT based simulation is smaller. This is reasonable, since at higher resolution there is more contribution from electrons scattered close to the nucleus, where bonding effects play a smaller role. Importantly, we note that a correct identification of B and N sites requires that the 1.08 Å reflection (rather than just the 2.16 Å as expected from IAM) is included into the image without any uncontrolled phase shifts. Hence, even if the 1.08 Å beam could be transferred in an experiment (it corresponds to a scattering angle of 40 mrad at 80kV), it is not obvious how one could separate the effects of electron optical aberrations from the intrinsic effect of the sample. As shown below, this is a complicated task already with only the first reflection, where one can use the bi-layer hBN regions as reference.

**IX. RESIDUAL ABERRATIONS VS. INTRINSIC CONTRAST**

For the case of hexagonal boron nitride, it is important to verify and compensate the effects of residual, non-round aberrations. In thin hBN samples, it is frequently possible to find a “reference” structure for this purpose just next to the single-layer membrane, which is a region of double-layer hBN. For the bi-layer area, a symmetric contrast for the two sub-lattices must be present already due to the symmetry of the material (B is above N in adjacent layers). The asymmetry in the experimental intensity profiles for the bi-layer region therefore shows exclusively the effect of residual aberrations. In a simplistic approximation, one might assume identical imaging conditions for these different regions of the sample, imaged simultaneously and separated by a few nm. However, this has never been verified with a sufficient precision.

Fig. 11 shows a quantitative analysis of this point. We define an “Asymmetry” value as the relative contrast difference between the two atomic sites, normalized to the total modulation. Under ideal imaging conditions, a symmetric profile (Asymmetry of zero) would be expected for double-
Asymmetry for ideal conditions:
Graphene: 0.00
h-BN double layer: 0.00
h-BN mono-layer IAM: 0.10
h-BN mono-layer DFT: 0.02

Asymmetry for ideal conditions:
Graphene: 0.00
h-BN double layer: 0.00
h-BN mono-layer IAM: 0.10
h-BN mono-layer DFT: 0.02

Figure 11: Asymmetry definition and measurement. (a) Definition of the “Asymmetry” value, as relative difference of the contrast on the two atomic sites (A, B), normalized to the total modulation (site C (the hole in the hexagon), minus the mean value of A and B). Without non-round aberrations, we expect a zero value for graphene and even-layered hBN, and a non-zero value for odd-layer hBN. (b) Experimental image of single layer graphene, recorded with the same conditions as our hBN data, and with similar signal to noise ratio. Insets show the clearly different images at separated positions. (c) Automated analysis of the asymmetry value for every unit cell, revealing the clear variation of this number across the image.

layer (or even-layered) hexagonal boron nitride regions, as well as for single-layer graphene. For single-layer hBN, one would expect an asymmetry of 0.10 from the independent-atom model, and 0.024 from the DFT based result. For triple-layer hBN, this relative asymmetry is expected as 0.033 from IAM, and 0.008 from DFT. Hence, it is also possible to discern between IAM and DFT from a single-layer - triple-layer comparison. We have implemented an automated method to measure this asymmetry for every unit cell (available as plug-in for the ImageJ software). The algorithm first locates all the intensity maxima, which represent the centers of the graphene or hBN hexagons. Then, it measures the intensity at these maxima (value C), as well as the intensity
on the atomic sites A and B (at a given distance and orientation relative to the hexagon centers). As shown in Fig. 11, the asymmetry value does vary considerably over the field of view, as can be easily verified using images from large clean areas of single layer graphene.

Now, we verify how the asymmetry for hBN depends on residual electron optical aberrations. We have tested all parameters up to third order aberrations. As examples, Fig. 12a shows simulated images for hBN in the presence of astigmatism (A1), two-fold astigmatism (A2), and coma (B2). As expected, the asymmetry depends on some of these values. However, the difference in the asymmetry from single-layer to bi-layer hBN is not sensitive to these effects. Thus, one would
always expect a sharp step in the asymmetry value when going from (n) to (n+1) layers in hBN according to IAM, and almost no difference in the DFT model, independent of small residual aberrations.

Fig. 12b shows the intensity profiles for the example with a two-fold astigmatism of 25nm. Here, the bi-layer profile was rescaled by a factor of 1/2, and the left sublattice was shifted to the same position. We then compare the contrast on the other sublattice (as in the experimental analysis, Fig. 5 of the main article). We find that contrast difference in this comparison is the same as under ideal imaging conditions, independent of small non-round aberrations. Hence, the exact agreement between single-layer and (rescaled) bi-layer hBN, as found in the experiment, confirms the DFT model and rules out the IAM, independent of small residual aberrations.

In addition, we have tested whether the asymmetry (or its variation) depends on sample tilt. We simulated HRTEM images of inclined graphene sheets (using standard multislice code [19] with each atom on a separate slice), and could not produce an asymmetry even for large tilts (up to 40°). Moreover, we have obtained experimental images of graphene membranes intentionally tilted (by 20°), and did not find any additional asymmetry, or a variation that would be correlated with the tilt direction. The variation in the surface normals in this type of samples is much smaller, below ca. 5° [20, 21].

Fig. 12c shows the image of a larger area of ultra-thin hBN, with the image section that was used in the main article indicated by a white box. Fig. 12d shows the asymmetry measurement on the entire area. One can see a smooth trend from the top left to the lower right corner of the image, within large regions of constant thickness, which must be the effects of varying imaging conditions. The asymmetry value is unreliable at point defects, step edges, and in the vacuum region, which however are clearly discerned in the original image. The single- and bi-layer regions that were analyzed in the main article are again indicated (solid white lines). Based on the large-scale trend, these regions were chosen in a way that differences from residual aberrations are minimized. The white dashed lines indicate contours of approximately constant asymmetry, with the asymmetry values differing by 0.1. This corresponds to the IAM difference. As shown in Fig. 12b, a change in two-fold astigmatism of 25nm can produce this amount of asymmetry. In any case, one can easily obtain this 10% difference as an artefact if the variation of imaging conditions is not quantitatively verified, already with single-layer and bi-layer reference region separated by only a few nanometers.

The automated analysis of the hBN images allows to verify our result for a larger amount of
Figure 13: Comparison of single- and bi-layer hBN based on the asymmetry measurement. (a) Experimental image, with single- and bi-layer area indicated. (b) Asymmetry measurement for every unit cell. Selected regions for the measurement, away from defects and step edges, are indicated. (c) Experimental image with measured asymmetry values and regions indicated. Given in parentheses is the standard deviation of the unit-cell asymmetry values. Note that the standard deviation is the statistical uncertainty of the individual unit cell measurement. The uncertainty of the mean values is better by a factor of at least 5 (for the smallest region with 25 unit cells). The single- and bi-layer images in this measurement differ in asymmetry by less than 0.03, which is also the variation between closely spaced areas of the same thickness. Hence, they are identical within experimental errors while the 0.1 difference from IAM can be ruled out.

data, which would be very tedious when using manually selected and averaged unit cells. Fig. 13 shows an example measurement for the comparison of single-layer and bi-layer hBN using the automated asymmetry analysis. The automated analysis provides the asymmetry value on every individual unit cell. It is then easy to extract the mean value and standard deviation (in this example using 25 or more unit cells in each indicated area). The areas are chosen such that defects, step...
Figure 14: Large-area hBN image, including a single-layer region (red) that is almost surrounded by a double-layer reference (blue). (a) HRTEM image (average of 30 exposures). The red and blue indicated regions did not change during the underlying image sequence. (b) Asymmetry measurement, showing the large scale variations of imaging conditions. White box indicates the region of interest for c-f. (c+d) Asymmetry measurement results. The mean asymmetry values and standard deviations are shown in the image (c), and regions for the corresponding measurements are shown in (d). All differences between the single-layer area and surrounding bi-layer region are significantly smaller than expected from IAM (Again, note that the standard deviation reflects the uncertainty for one individual unit cell; statistical uncertainty of the mean value is better by a factor of at least $\sqrt{25} = 5$). (e+f) Asymmetry measurement, with a value of 0.1 (as expected from IAM) manually added (e) or subtracted (f) on the single layer region: If the IAM were correct, we should clearly see such a step between single and double layer areas. Scale bars are 1nm.

edges, and areas where the thickness has changed during the image sequence are avoided. The identical asymmetry in single- and bi-layer regions is confirmed. This means that the images are identical except for a constant factor in the total contrast. Also, several measurements in an area
of constant thickness allow to further verify the error due to variations in imaging conditions.

A further example is shown in Fig. 14. Fig. 14a+b show the larger scale image and the asymmetry analysis on the entire area. In one corner of the image (Fig. 14a), we find a single-layer area that is almost surrounded by a double layer that may serve as reference. We can now easily measure the asymmetry and its standard deviation for the mono-layer and all surrounding bi-layer areas: Fig. 14c shows the image section with the result of the asymmetry measurements, while 14d shows the color-coded asymmetry image along with the chosen areas. From all measurements, it is clear that there is no intrinsic difference; the image of mono-layer hBN is exactly identical to double layer hBN with half the contrast. All differences between separated regions are exclusively due to the variation of imaging conditions across the field of view. In this example, a difference of 0.1 is obtained over a spatial separation of ca. 7nm (the two furthest separated measurements in the bi-layer region, Fig. 14c, differ by 0.08), while several single-layer/double-layer comparisons can be made on a much shorter distance in the same image.

Indeed, the difference in asymmetry as predicted by IAM simulations should be detectable at the present noise level already from visual inspection of the asymmetry images. To demonstrate this, we have manually added and subtracted 0.1 to the asymmetry value of single layer regions (Fig. 14e,f): If the IAM prediction were correct, one would see such steps very clearly, and this is not the case in any of our measurements. Also, the step between single/triple, triple/double or triple/quad layer hBN should be well visible: It is only smaller in numerical value in our relative definition of the asymmetry but in this value also the noise is equally smaller in thicker sample areas. Again, the automated analysis allows to screen larger amounts of data, monitor the variation of imaging conditions with time (in image sequences), and makes possible errors that may arise in the manual analysis of a singular measurement highly unlikely.

SUPPLEMENTARY INFORMATION


A1

SUPPLEMENTARY INFORMATION


Appendix 2

Simulation of bonding effects in HRTEM images of light element materials

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Simulation of bonding effects in HRTEM images of light element materials

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Abstract
The accuracy of multislice high-resolution transmission electron microscopy (HRTEM) simulation can be improved by calculating the scattering potential using density functional theory (DFT) [1,2]. This approach accounts for the fact that electrons in the specimen are redistributed according to their local chemical environment. This influences the scattering process and alters the absolute and relative contrast in the final image. For light element materials with well defined geometry, such as graphene and hexagonal boron nitride monolayers, the DFT based simulation scheme turned out to be necessary to prevent misinterpretation of weak signals, such as the identification of nitrogen substitutions in a graphene network. Furthermore, this implies that the HRTEM image does not only contain structural information (atom positions and atomic numbers). Instead, information on the electron charge distribution can be gained in addition.

In order to produce meaningful results, the new input parameters need to be chosen carefully. Here we present details of the simulation process and discuss the influence of the main parameters on the final result. Furthermore we apply the simulation scheme to three model systems: A single atom boron and a single atom oxygen substitution in graphene and an oxygen adatom on graphene.

Introduction
Conventional HRTEM image simulation so far neglects all kinds of interatomic interactions within the specimen by calculating the total specimen potential as a superposition of isolated atom potentials [3]. It is generally known that the state of an atom is, of course, influenced by its environment and hence techniques that are more sensitive to changes in the electronic
state, such as electron energy loss spectroscopy [4] or scanning tunneling microscopy [5], make use of advanced simulation methods to model the specimen.

In 1997, Gemming and Möbus performed ab-initio HRTEM simulations of ionic crystals and justified the use of conventional image simulation [1]. About ten years later, and after enormous improvement in electron optics and the resolution of the TEM by means of aberration correction [6,7], Deng et al. [2,8] performed DFT based HRTEM calculations for bulk oxides and found that chemical bonding should be detectable and in practice is hindered only by the poor specimen quality obtained by ion-beam thinning. Furthermore they pointed out that it is possible to study charge transfer by other techniques such as convergent beam electron diffraction [9,10] but all methods available can only offer global information as they observe the charge distribution in reciprocal space. In contrast, the observation of the same effect in real space using HRTEM would result in local information, which would open new frontiers for electron microscopy [2,11].

Previous studies were focused on bulk oxides, because they are known to have strong ionic bonds. Our target materials, in contrast, are two dimensional crystals such as graphene and hexagonal boron nitride as they offer an outstanding specimen quality that has not been achieved for bulk materials so far: Their thickness is perfectly defined (one atomic layer) and it is possible to find areas without defects and without amorphous top and bottom layers. Furthermore both of our target materials are built from exclusively light elements where strong bonding effects can be expected because most of their electrons are valence electrons. Another important factor for the experimental detection of these effects in HRTEM is that the contrast of boron, carbon, nitrogen and oxygen is almost identical under our imaging conditions [12] (shown by the black curve in Figure 1). Hence even small contrast variations are relatively easy to detect.

Due to these improvements in specimen quality, for the first time, we were able to measure the influence of charge redistribution on the HRTEM image contrast experimentally for two different materials, namely nitrogen doped graphene and single-layer hexagonal boron nitride [13]. This result has two important implications: First, chemical bonding gives small corrections to the atomic contrast in the TEM, which has to be kept in mind whenever weak signals are analyzed. Second, and probably more importantly, the HRTEM image is not only governed by structural information but also contains information about the electronic state of the specimen. This allows the study of the electron charge distribution in point defects and other nanoscaled objects that can not be accessed by diffraction experiments.

Here we give detailed information on the DFT based simulation used in [13] and explain the analysis for three model systems: A single atom boron and a single atom oxygen substitution in graphene and an oxygen adatom on graphene.

Experimental

Modeling the HRTEM image formation

High resolution TEM image simulation can be separated in three main parts: First the interaction between the incident elec-
Simulation of bonding effects in HRTEM images of light element materials


The interaction with the specimen is described by a very simple scattering process where the incident high energy electron is scattered by the combined Coulomb potential of all atomic nuclei and electrons within the specimen. Mathematically one has to solve a relativistic version of the Schrödinger Equation 1, where $\Psi(\vec{x})$ is the wave function of the electron at position $\vec{x}$, $m$ is the relativistic mass of the electron and $V_x(\vec{x})$ is the specimen potential.

$$\left(-\frac{h^2}{2m} \nabla^2 - eV_x(\vec{x})\right) \Psi(\vec{x}) = E\Psi(\vec{x}) \tag{1}$$

In the limit of high energy electrons, backscattering can be neglected and Equation 1 can be solved using the multislice algorithm. In this study we focus on single layer materials of light elements. Hence the exit wave can be calculated (in a single-slice approximation) by Equation 2, where $\sigma$ is the interaction parameter and $V_x$ is the projected specimen potential [3].

In addition, for these structures and our imaging conditions, it turned out that the linear image approximation (Equation 3) is justified, as found by comparison of the result with the standard calculation. The amplitude spectrum of the wave in the imaging plane $I_{\text{image}}(q_x,q_y)$ can be derived from the Fourier space specimen exit wave $\Psi_{ex}(q_x,q_y)$ by multiplication with the objective lens phase factor function $exp[2\pi i f(q_x,q_y)]$, where $f(q_x,q_y)$ depends on the defocus $\Delta f$, spherical aberration $C_s$ and higher order aberrations [14]. The exact expression of $f(q_x,q_y)$ can be found in [16]. Because the structures studied here are weak scatterers, the linear imaging condition is justified and, for an incident plane wave, the final image intensity is given by Equation 5 [14].

$$I_{\text{image}}(x,y)=1+2\sigma FT^{-1}\left[\sin\left(\chi(q_x,q_y)\right)\cdot FT\left[\Psi_x(x,y)\right]\right]$$

Of course this is a very simple model of the real scattering process, which neglects all kinds of inelastic processes by assuming that the state of the specimen is not at all influenced by the presence of the high energy electrons. Nevertheless, it is well established for HRTEM simulation and in this work we use exactly the same framework (with all its limitations) but focus on a very fundamental question: How do we obtain the scattering potential? The standard approach is to calculate the total specimen potential as a superposition of isolated atom potentials, which have been calculated previously for each element by solving the quantum many body problem for all electrons and the nuclei of a single atom. One example are the potentials published by Doyle and Turner in 1968 [17]. Their paper was based on atomic potentials obtained by relativistic Hartree–Fock self-consistent field calculations performed by Coulthard in 1967 [18], where the main assumption was that the atomic charge distribution is spherically symmetric.

A more accurate way is to include electronic interactions between atoms in the specimen by DFT. In this way, ionic atoms with non-spherical electron distributions can be modeled without any a priori knowledge.

**How to obtain DFT potentials**

The DFT calculation was performed in two steps: First we performed a structure optimization of an initial atomic configuration by using the very fast and efficient pseudopotential DFT code VASP [19]. Unfortunately it was not possible to extract the total electrostatic potential directly from the pseudopotential calculation as it only offers the self consistent valence charge density but the total charge density is needed. Hence, in a second step, we used the relaxed structure to set up an all electron DFT calculation, and therefore we used the WIEN2k [20] DFT software. Furthermore, WIEN2k has the significant advantage that, besides offering access to the total electron charge density and corresponding X-ray scattering factors, in addition, the calculation of the total Coulomb potential (including all electrons and nuclei within the unit cell) is already implemented. Deng and Marks [8] used the X-ray scattering factors, while our method directly makes use of the available potential file.

A very important cross-check is to compare the WIEN2k potential to other potentials used in HRTEM simulations. This is easy to achieve, because the starting point for the DFT calculation (before the first iteration cycle) is also built up from isolated atom potentials, and the subsequent iteration process, searching
Figure 2 WIEN2k starting potential (red) compared to Doyle–Turner (black) and Kirkland (green) potentials. The WIEN2k potential was obtained by putting a single carbon atom into a 10 Å × 10 Å × 10 Å unit cell and calculating a linescan of the electrostatic potential with a resolution of 250 points per Angstrom (ppÅ). Far from the core, the WIEN2k potential approaches a non-zero constant value. In order to obtain the usual normalization, the potential was shifted (i.e., smallest value was set to zero).

The 3D unit-cell potential is stored in the file case.vcoul and WIEN2k comes with utility software (lapw5 and lapw5c) to extract linescans and 2D slices from this file. Hence a point grid of the 3D potential can be extracted by combining subsequently calculated 2D slices using the wien2vens script written by Masao Arai [21]. Difficulties arise from the fact that the potential is divergent near the positions of the atomic nuclei but equidistant discretization is performed. Furthermore the total number of sampling points is rather limited due to limited computer time. Usually this sampling problem is overcome by smoothing the analytical 3D potential before the discretization is performed and, in this way, a much smaller sampling rate can be used (typically 10 ppÅ). In Figure 2 this smoothing can be seen very well in the case of the Doyle–Turner potential, which is not divergent near the nucleus. However, in practice this was not possible here because we can only access the WIEN2k potential via the utility software.

We analyzed the sampling error in more detail by comparing the dependence of the projected potential from the position of the sampling point at a constant sampling rate of 30 ppÅ in the z-direction (parallel to the incident beam), which turned out to be a realistic compromise, but a much higher rate in the perpendicular direction. After projection along the z-direction, this results in the projected potential printed in green in Figure 3. From this it is possible to study the error that is made when this function is discretized using a smaller number of sampling points.

The blue boxes in Figure 3 indicate the mean value within one pixel at a resolution of 30 ppÅ, which corresponds to the ideal value within this quadrant. Hence the deviation from the top of the blue box indicates the sampling error. Interestingly, for 30 ppÅ, the sampling error is significant only for the center pixel and is caused by a single value in the 3D potential. We use a very simple method to handle this problem: Whenever a value in the 3D potential is higher than some cutoff value, we change this value to the highest value in the neighboring pixels. In this way the obtained projected potential value of the central pixel is in the range of the ideal value within a factor of three, instead of being off by up to two orders of magnitude (compare red and green curves in Figure 3). This very crude approach can be used, because the fraction of the intensity that interacts with this part of the potential remains negligibly small.

In order to be more flexible, we modified the wien2vens script: First, we included the possibility to shift the slicing volume with respect to the DFT unit cell. In this way it is possible to avoid sampling points very close to the nuclei. Second, it is now possible to slice sub-volumes. This can be used to speed up the calculation, because several sub-volumes can be sliced at the same time and vacuum regions can be skipped. The modified version of the script can be found in the Supporting Information (Supporting Information File 2).
Once an accurate 3D potential is obtained and renormalized it can be used for TEM image simulation. Thereby each direction of the incident beam can be modeled by rotating the 3D potential using linear interpolation algorithms.

Influence of DFT parameters
In order to set up meaningful DFT calculations, it is always necessary to do convergence tests of the main parameters such as k-points and basis set size [22]. Usually the convergence is tested with respect to the total energy and the electric field gradients. This was done using ideal graphene as a test structure. Interestingly, we find that the main quantity that we are interested in, i.e., the projected electrostatic potential, is not very sensitive to the DFT input parameters: The absolute differences between the DFT and IAM potentials are in the range of 10–30% where the influence of the DFT parameters is smaller than 1.5% (for details see Supporting Information File 1).

Example calculation
As we expect bonding effects to be strongest in exclusively light element materials, we applied this simulation scheme to different types of defects in graphene. The single atom substitutions, where one carbon position is occupied by another atomic species, turned out to be the ones that can be most easily accessed experimentally because the graphene structure remains almost undisturbed. Hence, bonding effects can easily be separated from structural changes by analyzing the deviations from the regular lattice contrast. For vacancies and adatoms the contrast analysis is much more difficult, due to changes in both, structural and electronic configuration. Nevertheless, the influence of chemical bonding on the final TEM image can be detected for all of them.

Boron and oxygen substitution in graphene
The structure models obtained from the VASP relaxation are shown in Figure 4. Details on the relaxation process can be found in the supplementary information of [13].

The WIEN2k calculation for the boron substitution was performed using the generalized gradient approximation (GGA) for the description of the exchange-correlation effects [23] with the following set of technical parameters: Separation energy $-5.5$ Ry, $6 \times 6 \times 1$ k-points, RKMAX = 7 and GMAX = 12. For the calculations including oxygen atoms, the parameters were modified to: $-6$ Ry, $4 \times 4 \times 1$ k-points, RKMAX = 8 and GMAX = 16. Both calculations were performed in a spin-polarized fashion, and the linearization energies were set automatically.

The effect of charge redistribution due to chemical bonding can be studied by comparing the initial charge density (before the first iteration cycle, labeled IAM) and the self-consistent charge density after the WIEN2k calculation has converged (labeled DFT). The same is done for the potentials. This approach has the advantage that subsequent processing steps, such as the TEM image simulation, influence the quantities obtained by IAM and DFT in exactly the same fashion. The only difference is that the latter includes chemical bonding while the former does not.
Figure 4  Relaxed structure model of boron and oxygen substitution in graphene. Bond lengths are given in Å.

The 3D potentials were sliced with a resolution of 30 ppÅ, normalized and projected along the z-direction using a cutoff of −50 kV, as described above. The same was done for the all-electron charge density (stored in the file clmsum) where the renormalization and the cutoff was skipped.

In Figure 5 we analyze the difference in the charge density. In the difference images (panel c and h) the sp² hybridization of the graphene lattice is clearly visible by the dark contrast between the carbon atoms meaning that the charge density of the bonded configuration is increased in this area. Interestingly,
for the boron as well as for the oxygen substitution we find big differences in the charge density at the three neighboring carbon atoms, whereas the substitution atom itself remains almost neutral. After removing the periodic signal from the difference images, using a Fourier filter (panel d and i), a dipole shaped rearrangement of the electrons at the carbon atoms next to the substitution is detected. Comparing the boron and oxygen case we find that the polarization of the carbon atoms is almost exactly opposite: The electron density in the area surrounding the boron atom (green hexagon) is increased, whereas the oxygen atom is decreased. This should result in a decrease of the boron potential due to stronger shielding of the core potential and reduced contrast in the TEM image. For oxygen, on the other hand, we expect to have a stronger signal in the TEM image due to weaker shielding.

This is exactly what we find when analyzing the projected potentials. Dark contrast in the filtered difference images in Figure 6 corresponds to a decreased projected potential in the bonded configuration. The increase of the oxygen and the decrease of the boron potential (compared to the IAM) is clearly visible. Besides these obvious differences two more subtle conclusions can be drawn from the potential analysis. First, we find that, also for the potential, the difference is not sharply located at the position of the substitution atom but instead spreads over further atomic distances. This results in low frequency information about the defect. The transfer of this information can be enhanced in the TEM by working at higher defocus. Second, for both cases the total potential is decreased by about 15% (see total change in panel e and j of Figure 6). This change in the mean inner potential is well known and was previously studied for semi-conducting materials by Schowalter et al. [24]. For ideal graphene we find a difference in the mean inner potential of 15.5%. Interestingly this results in an overall loss of contrast in the final TEM image of approximately 8%. However, this is only a minor contribution to the Stobbs factor [25], which is in the range of 50–80% and is used to fit simulated and experimental TEM image intensities.

After analyzing the DFT results we now want to study how the charge redistribution influences the observed contrast in the final TEM image, which is obtained by applying Equation 5. This calculation was performed for two different values of defocus: Scherzer defocus \( f_1 = -9 \text{ nm} \) and \( f_2 = -18 \text{ nm} \), where the graphene lattice reflection is in the second extremum of the CTF. The former is the standard condition for high resolution TEM, whereas the latter offers better transfer of low spatial frequencies resulting in enhanced contrast of the substitution

![Boron substitution in graphene](image1)

![Oxygen substitution in graphene](image2)

Figure 6  Analysis of the projected potential of the boron (top) and oxygen substitution in graphene (bottom line). a) and b) show the projected potential of IAM and DFT in logarithmic scaling, where the absolute difference image c) is displayed on a linear greyscale. Dark contrast in c) and d) corresponds to a decrease in the projected potential in the bonded configuration due to stronger shielding of the nuclear potential by electrons. The changes of the potential inside the marked areas in c) are given in e). Because the total potential is changing it is easier to compare relative differences. f–j) show exactly the same analysis for the oxygen substitution. Scale bars are 1 Å.
defects. The other parameters were: High tension 80 kV and spherical aberration \(C_s = 0.02\) mm. Higher order aberrations were not taken into account in this study.

The resulting micrographs for the boron substitution are shown in Figure 7. From this we see that the chemical bonding results in weaker contrast of the boron atom. This simplifies the detection of the substitution atom already at Scherzer defocus because the contrast difference between boron and the carbon atoms of the graphene lattice is increased from 5% for neutral atoms (IAM) to 9% in the bonded configuration (DFT). According to the DFT result this difference should be further pronounced by working at higher defocus, which is shown in the lower part of Figure 7.

For the oxygen substitution, shown in Figure 8, we find similar relative contrast changes but reach opposite conclusions, because the polarization of the carbons in the DFT calculation...
prevents the detection of the oxygen atom in the carbon network, whereas this should be possible according to the IAM result. This may be the reason why we did not detect residual oxygen atoms in reduced graphene oxide [26].

Oxygen adatom on graphene
The relaxation process resulted in an oxygen atom located at the bridge position between two carbons. The two carbon atoms are bent out of plane by approximately 0.4 Å. The C–C bond is stretched to 1.52 Å and the C–O distance is 1.47 Å, which is in good agreement with previously reported structures [27].

From analysis of the 3d densities, we found a very interesting charge redistribution in the out-of-plane directions, as can be seen in Figure 9. However, this direction cannot be accessed in a viewing direction orthogonal to the graphene plane.

The TEM simulation for normal incidence of the electron beam is shown in Figure 10. Again, the charge transfer around the oxygen atom would be very difficult to detect in a Scherzer defocus image. However, it might be discernable, if the lower spatial frequencies are included in the image. Under the assumption that the oxygen adatom remains stable enough under the electron beam to obtain a sufficient high signal to noise ratio, this might be achievable by applying higher defocus (see second row in Figure 10) or a phase plate (see third row in Figure 10).

Conclusion
We presented a practical method to include chemical bonding in the HRTEM image simulation process using DFT based scattering potentials recently applied in [13]. Hence, an all-electron calculation was set up based on a previously relaxed atomic configuration. As we have shown the WIEN2k software is well suited for this task as the initial potential is in good agreement with commonly used scattering potentials and the subsequent iteration process acts as a relatively minor perturbation. The potential itself is not very sensitive to the DFT input parameters. However, as the electrostatic potential is divergent at the position of the atomic nuclei, care has to be taken during the discretization process. We found that a sampling rate of 30 ppÅ in combination with a cutoff method produced reasonably accurate results. This 3d potential can subsequently be used for multislice TEM simulation, however this was not necessary for the single layer materials studied here. The influence of chemical bonding can be analyzed by comparing the IAM charge density, corresponding potential and TEM image with those obtained from the DFT calculation.

This analysis was demonstrated for the substitutions of a single boron and a single oxygen atom in graphene as well as for an oxygen adatom on graphene. The relative changes are very similar to the ones we found previously for the single atom nitrogen substitution [13], where we were able to validate the advantage of the DFT calculation over the isolated atom model experimentally. For the oxygen substitution we find exactly the same situation as for the nitrogen defect: The electron charge density in the area surrounding the substitution is decreased due to polarization of the neighboring carbons, resulting in weaker shielding of the core potential and increased TEM contrast of the substitution atom. For boron the situation is exactly the inverse. However, the implication on the final TEM image

![Figure 9](image-url)  
*Figure 9* Difference between the 3d electron charge density (center column) and the 3d electrostatic potential (right column) between IAM and DFT for an oxygen adatom on graphene. The top row is for armchair and the bottom row for zig-zag direction. An increase in electron charge density (potential) due to chemical bonding appears as dark (bright) contrast in the difference image.
We conclude that chemical bonding must be included in comparative HRTEM image simulations whenever very small signals are analyzed. Here we want to emphasize that the key requirement for this kind of analysis is the well defined specimen geometry rather than the single layer thickness of the model systems used in this study. Earlier calculations showed that, whenever a high enough experimental accuracy is achieved, bonding effects should be detectable for a wide variety of materials [2,8]. This offers the possibility to gain...
experimental insight into the electronic charge distribution of the specimen at the atomic scale by HRTEM.

Supporting Information
Supporting Information File 1
WIEN2k convergence tests for ideal graphene
[http://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-2-45-S1.pdf]

Supporting Information File 2
Program to get 3D WIEN2k potentials (Phyton script, rename to .py).
[http://www.beilstein-journals.org/bjnano/content/supplementary/2190-4286-2-45-S2.txt]

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Appendix 3

Stone-Wales-type transformations in carbon nanostructures driven by electron irradiation

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I. INTRODUCTION

The Stone-Wales defect—SW(55-77)—is the simplest example of topological disorder in graphene and other sp2-hybridized carbon systems. It can be formed by rotating a C-C bond by 90° with regard to the midpoint of the bond—referred to as the SW transformation—so that four hexagons are turned into two pentagons and two heptagons. This defect has received a considerable amount of attention because it has the lowest formation energy among all intrinsic defects in graphenic systems, and because it presumably plays an important role in plastic deformation of carbon nanotubes (CNTs) under tension by relieving strain. It can also act as a source for dislocation dipoles.

Regardless of being the lowest-energy defect in graphene and other sp2-hybridized carbon nanostructures, SW(55-77) needs about 5 eV to appear in graphene and 3-5 eV in CNTs with a diameter above 1 nm, which should lead to a negligible equilibrium concentration of such defects at room temperature. However, recent advances in high-resolution transmission electron microscopy (HRTEM) have allowed the identification of such defects in graphene and CNTs.

Moreover, SW transformations play an important role in the response of graphene to electron irradiation, leading to changes in the morphology of vacancy-type defects and to their migration. Such changes are equally surprising because the barrier for bond rotation is about 5 eV, which should exclude thermal activation as a cause for SW transformation at room temperature during experimentally relevant time scales.

Regarding irradiation effects, previous simulations showed that an energy of ~30 eV must be transferred to a C atom in graphene in the in-plane direction for a bond rotation to occur. Also, this cannot explain the frequently observed SW transformations under the usual transmission electron microscopy (TEM) imaging conditions, since with typical acceleration voltages (~500 kV) the transferred kinetic energy in the direction almost perpendicular to the electron beam will remain significantly below 10 eV.

Here, by combining aberration-corrected (AC) HRTEM with atomistic computer simulations, we show that topological defects associated with the SW transformation can be formed in sp2-hybridized carbon nanostructures by impacts of individual electrons at energies even below the threshold for atomic displacements. We further study in detail the mechanisms of irradiation-driven bond rotations and explain why electron irradiation at moderate electron energies (~100 keV) tends to amorphize rather than perforate graphene. We also show via simulations that Stone-Wales defects can appear in curved graphitic structures due to incomplete recombination of irradiation-induced Frenkel defects, similar to the formation of Wigner-type defects in silicon.

II. METHODS

A. Experimental Methods

Graphene membranes used in our experiments were prepared by mechanical exfoliation of graphite on Si/SiO2 substrates and transfer of the resulting graphene sheets onto TEM grids as described previously. For TEM experiments we used an FEI TITAN 80–300 equipped with an image-side aberration corrector and operated at 80 kV. The spherical aberration was set to 15 μm and images were recorded at the Scherzer defocus. The extraction voltage of the source was reduced to 2 kV and the condenser lens C2 was switched off in order to minimize the energy spread. Under these conditions, dark contrast in the images can be directly interpreted in terms of the atomic structure. Image sequences were recorded on a CCD camera with exposure times of 1 s and intervals of approximately 2 s.

B. Computational Methods

We carried out atomistic computer simulations based on spin-polarized density functional theory (DFT) implemented in the plane wave basis set VASP code. The projector-augmented wave potentials were used to describe the core electrons, and the generalized gradient approximation of Perdew, Burke, and Ernzerhof was used for exchange and correlation.
correlation. We included plane waves up to a kinetic energy of 300 eV. The \( \mathbf{k} \)-point sampling of the Brillouin zone was performed using the scheme of Monkhorst-Pack\(^\text{24} \) for the periodic dimensions. Structure relaxation calculations were combined with molecular dynamics (DFT-MD) simulations with a lower kinetic energy threshold and fewer \( \mathbf{k} \) points.

Due to the high computational cost of the DFT-MD method, only a few simulations were carried out at this level. Whenever statistics needed to be gathered, we calculated the forces using the nonorthogonal DFT-based tight binding (DFTB) method.\(^\text{23} \)

The main results were checked against DFT-MD. In total, we carried out \( \sim 27,000 \) dynamical DFTB-MD simulations. The simulated structures consisted of 120–200 atoms and were fully optimized. For the displacement threshold simulations, one of the atoms was assigned a kinetic energy \( T \) with the initial velocity vector pointing to a preselected direction. The initial temperature of the system was set to 5 K, although we observed no differences when carrying out the simulations for initially stationary atoms. Displacement threshold \( T_d \) (minimum kinetic energy required to eject the atom) was found to be 22.50 eV, in a good agreement with earlier DFTB results.\(^\text{26,27} \) It is also close to the DFT value (22.03 eV).\(^\text{28} \) For the annihilation simulations, various system temperatures were studied (500–1200 K) both to fasten the migration of the adatoms and to understand the effect of an elevated temperature (as will be mentioned below).

### III. RESULTS AND DISCUSSION

#### A. Stone-Wales defects due to single-electron impacts

We begin the presentation of our results with the description of experimental observations of SW(55-77) in HRTEM images. Several long image sequences, typically containing hundreds of images from clean and initially defect-free graphene membranes, were recorded at 80 kV. Occasionally, SW(55-77) defects appeared in individual exposures, as in the example shown in Fig. 1(b) [Fig. 1(c) with structure overlay]. Remarkably, in most of the observed cases, isolated SW(55-77) appeared in pristine graphene for one 1 s exposure only to disappear in the following frame. Hence, the lifetime of this defect under the 80 kV electron beam in terms of irradiation dose is of the order of \( 1 \times 10^7 \) electrons/\( \mu \text{m}^2 \), the dose used for a single exposure.

To understand the appearance and disappearance of SW(55-77), we carried out atomistic simulations for individual displacement events under the electron beam. After calculating \( T_d \), we extended this calculation to all in-plane (\( \phi \) and \( \theta \)) and out-of-plane angles in the range \( \theta \in [0^\circ, 25^\circ] \); see Fig. 2. Displacements with \( \theta > 25^\circ \) would result in transferred kinetic energies of more than 2 eV below \( T_d \) for an electron beam even at 120 keV. Since the displacement threshold increases for increasing \( \theta \), it is unlikely that this restriction would lead us to miss any significant electron-beam-induced structural changes, especially for electron energies similar to those used in this study (80 keV). The calculated displacement thresholds are shown in Fig. 2 in a relative scale along with the space angles for which we observed impact-induced SW transformations.

![FIG. 2. Relative displacement threshold \( T_{d,\phi,\theta} / T_d \) as a function of the displacement space angle (\( \phi, \theta \)). Crosses mark the angles for which we observed formation of SW(55-77).](image)

It is evident from Fig. 2 that the SW transformation is a very likely event at displacement angles slightly away from the graphene plane normal (\( \theta \approx 2.5^\circ \)). The transferred kinetic energies (\( T \)) required by this process are below the displacement threshold for the corresponding \( \phi \) and \( \theta \) \( (T_{d,\phi,\theta}) \) since no actual removal of the recoil atom is necessary for the bond rotation to occur. Typically, \( T \approx T_{d,\phi,\theta} - 1 \) eV resulted in SW(55-77) formation, although for some space angles even \( T \approx T_{d,\phi,\theta} - 2 \) eV was enough. The probability for SW(55-77) formation is particularly high for certain space angles, which is related to different mechanisms of SW transformation, as described below.

The above-presented result is in clear contrast with the earlier simulation results for graphite,\(^\text{29} \) where no SW(55-77) formation was observed for low \( \theta \). This discrepancy is caused by the neighboring graphene planes in the case of graphite: The displaced atom gets attached to the adjacent layer and...
example cases are for the same nudges the neighbor to cause the bond rotation. Note that the interplay of all three variables (unreasonably high computational cost. we did not study this process in nanotubes at length due to introduced for quantitative analysis of SW transformation, two new parameters (tube diameter and chirality) should be

shows the two processes which account for the majority of the SW transformations observed during our simulations. In the “circle” process [Fig. 3(a)], the displaced atom circles around its neighbor, whereas in the “nudge” process [Fig. 3(b)] it nudges the neighbor to cause the bond rotation. Note that the example cases are for the same \( \theta \) and almost same \( T \), but for different \( \phi \). The resulting process for each displacement is an interplay of all three variables (\( T, \theta, \phi \)).

Similar mechanisms also exist for CNTs. However, as two new parameters (tube diameter and chirality) should be introduced for quantitative analysis of SW transformation, we did not study this process in nanotubes at length due to unreasonably high computational cost.

B. Annihilation of vacancies and adatoms with possible formation of SW(55-77)

Since we frequently observed formation of vacancy-adatom pairs (adatoms play the role of interstitials in graphene and CNTs) in our simulations of electron impacts onto graphene and earlier in CNTs, we also explored another possible mechanism of SW(55-77) formation, which is based on “incomplete” annihilation of a Frenkel defect. This study was motivated by the peculiarities of the recombination of such a defect in bulk silicon. In that covalently bonded material the recombination can give rise to either annihilation of the defect and restoration of the perfect crystal lattice or to a Wigner-type defect. Such topological defects are imperfections in the crystal lattice with the locally “correct” number of atoms (as opposed to vacancies and interstitials), with the atomic configuration separated from the perfect structure by a finite potential barrier. Such defects are also deemed to exist in graphite, \( \text{C}_{2} \) and SW(55-77) can clearly be classified into this group.

While carbon adatoms on graphene and CNTs (especially those inside nanotubes) are mobile at room temperature, they can easily find vacancies in the system and annihilate. Indeed, we occasionally observed disappearance of vacancies in HRTEM image sequences. Figure 4 shows an example of a monovacancy that disappears during observation. This proves that mobile carbon atoms are present under our experimental conditions and may recombine with vacancy-

FIG. 3. Typical SW transformation processes for low out-of-plane displacement angles (\( \theta < 25^\circ \)): (a) The “circle” process and (b) the “nudge” process. The black spheres correspond to the recoil (displaced) atoms, and the monovacancy structure is highlighted with numbered carbon rings in the second panels. The last panel shows schematically the route of the displaced atom. (See also videos S8 and S9 in Ref. 29.)

does not therefore initiate a bond rotation. In Fig. 3 we show the two processes which account for the majority of the SW transformations observed during our simulations. In the “circle” process [Fig. 3(a)], the displaced atom circles around its neighbor, whereas in the “nudge” process [Fig. 3(b)] it nudges the neighbor to cause the bond rotation. Note that the example cases are for the same \( \phi \) and almost same \( T \), but for different \( \theta \). The resulting process for each displacement is an interplay of all three variables (\( T, \theta, \phi \)).

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FIG. 4. (Color online) Experimental image sequence of a vacancy annihilation. Panel (a) shows a \( V_{5}(5-9) \) monovacancy, with an overlay in the inset, and (b) shows the same region in a later exposure, with no defect visible. Scale bar is 1 nm. (See also video S7 in Ref. 29.)

type defects. However, we never noticed the creation of an SW(55-77) after an observed monovacancy.

To simulate the annihilation process, we created nearby Frenkel defects (separated by a few Ångströms) in a graphene layer and small (6,6) zigzag and (10,0) armchair CNTs (radii \( r \approx 4.1 \text{ Å} \) and \( \sim 3.9 \text{ Å} \), respectively). We then heated the structures and collected statistics on the evolution of each system by running dynamical atomistic simulations at various temperatures (500–1200 K). Three possible outcomes emerged from the simulations: (1) perfect annihilation to the pristine structure (similar to the experimental images in Fig. 4), (2) formation of an SW(55-77) [Fig. 5(a)] and, surprisingly, (3) spurring of a \( \text{C}_{2} \) dimer with a remaining reconstructed divacancy \( V_{2}(5-8-5) \) [Fig. 5(b)].

For graphene, we always observed perfect annihilation in accordance with the experiments. However, if the adatom in graphene was placed on top of one of the two bonds in the nine-membered carbon ring which are right next to the pentagon, an SW(55-77) was spontaneously formed without an energy barrier. Thus, SW(55-77) may also form in graphene due to recombination of Frenkel defects, but the probability for this process must be much lower than in CNTs.

For (10,0) CNTs, we obtained perfect annihilation in approximately 54% of cases, SW(55-77) was formed in approximately 34% of cases, and dimer spurring occurred in approximately 12% of cases. For (6,6) CNTs, the values were 53%, 42%, and 4%, respectively. With increasing temperature the probability to sputter a dimer showed a slight tendency to increase. We also ran the calculations for an (8,8) CNT

FIG. 5. (a) SW(55-77) creation process as an outcome of a vacancy-adatom annihilation in a (6,6) armchair nanotube. (b) Carbon dimer spurring process in a (10,0) zigzag nanotube. The black spheres stand for adatoms and the gray ones denote the dimer to be sputtered [marked in the first panel of (b)]. The nanotube structures are shown from inside the tube. The tube axis is in the horizontal direction. (See also videos S10 and S11 in Ref. 29.)
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(r ≈ 5.4 Å) at 800 K in order to estimate the curvature dependency of the results. The values did not significantly differ from those for the (6,6) CNT, except for a somewhat increased tendency to perfect annihilation and decreased sputtering (with probabilities of 56% and 2%, respectively).

The formation energy of a spatially separated Frenkel defect in graphene within the DFTB model is approximately 11.1 eV. Transformation to form an SW defect from this initial setup leads to an energy gain of 5.4 eV. By sputtering a dimer, graphene would instead gain 0.4 eV. Hence, all three observed outcomes are also energetically reasonable for graphene. For nanotubes, the formation energies of both SW(55-77) and a divacancy are lowered due to the curvature and stronger C-C bonds at pentagons. The corresponding energy gains are also higher, which can explain why the probability for SW(55-77) defect formation and dimer ejection is higher in curved carbon nanostructures. The actual energies depend on the local curvature. It is also plausible that the dimer evaporation process plays a role in shrinking fullerenes under electron irradiation.16

C. Stone-Wales transformations in vacancy-type defects

The SW(55-77) defect represents the elementary case of a topological change in the graphene structure (i.e., a single bond rotation in an otherwise perfect structure). More abundant, however, are changes in the atomic configuration through bond rotations in the reconstructed vacancy defects, as recent experiments indicate.14,15 In the presence of a (multi)vacancy, the atomic configuration of a defect can be transformed between different metastable structures via bond rotations. It was presumed14 that such SW transformations of vacancy-type defects would be stimulated by electron impacts, but the actual atomistic mechanism has not been hitherto unraveled.

In order to get microscopic insight into irradiation-stimulated bond rotations near vacancy-type defects in graphene, we carried out a set of experiments and dedicated simulations aimed at assessing the probability of SW transformations in the defect structures. In our experiments, we initially generated “defective” graphene by brief 150 kV electron irradiation and then recorded image sequences of divacancies using 80 kV AC-HRTEM. As observed previously,14 the vacancies can transform between different configurations under the influence of the 80 kV electron beam. Moreover, the divacancies migrate and transition between the different reconstructed configurations via SW transformations, typically until they cluster into larger defects (see videos S5 and S6 in Ref. 29).

In Fig. 6, we show an example of a divacancy defect that transforms between different reconstructed shapes (V(5-8-5), V(555-777), V(5555-6-7777)) under the electron beam. The changes in the atomic structure of these divacancy configurations can be described by SW transformations at the defect. Moreover, multiple transformations allow migration of the divacancy. Similar to the SW(55-77) defect formation discussed above, the activation energy for these transitions is far too high to allow a thermally activated process with an observable rate at room temperature. Hence, on the basis of the observations, the activation energy for the transition must be provided by the electron beam.

In order to confirm that the SW transformations at these defects are caused by individual electron impacts, we carried out atomistic simulations of such impacts onto atoms near divacancies. Due to the computational cost related to many nonequivalent atoms present in the system and a large number of possible atomic configurations, we could not repeat the detailed analysis of the role of initial space angle of the displacement similar to pristine graphene, and we therefore limited our simulations to the θ = 0° case for all nonequivalent atoms at reconstructed divacancy structures. However, because the defects break the symmetry of the lattice, a directional preference for the displacements arises (displacement of an atom in the perpendicular direction will change its direction due to local strain). This effect is strong enough to facilitate bond rotations in reconstructed divacancy structures. In Fig. 7 we present examples of such processes for both V(5-8-5) → V(555-777) and V(555-777) → V(5555-6-7777) transformations.

FIG. 6. (Color online) Experimental images illustrating SW transformations in the atomic structure of divacancies and migration of these defects. Panels (a)–(d) show sequential HRTEM images of the same defect (in the lower row with structure overlay). (a) V(5555-6-7777) transforming into V(555-777) (b) and V(5-8-5) (c). Each of these transitions can be explained by a single bond rotation. In the later frame (d), the defect is again a V(5555-6-7777), but shifted by one lattice parameter. Scale bar is 1 nm. (See also videos S2–S4 in Ref. 29.)
Within these simulations, we never observed $V_2(555-777) \rightarrow V_2(5-8-5)$ transformations. Because the symmetry of the $V_2(555-777)$ defect around the middle atom is the same as that of pristine graphene [the middle atom is represented as a black sphere in the last panel of Fig. 7(a)], one would also expect that a $\theta \neq 0^\circ$ displacement is required for this transformation, similar to the SW(55-77) case, although in principle the surrounding atoms could also cause this transformation. We noticed that the most likely divacancy transformation, at least for $\theta = 0^\circ$, is $V_2(555-6-777) \rightarrow V_2(555-777)$. The $V_2(5-8-5) \rightarrow V_2(555-777)$ transformation was the least likely one of those observed. We never observed a $V_2(5-8-5) \rightarrow 2 \times (5-7)$ transformation\(^{14}\) during our simulations, which we also attribute to the limited simulated conditions ($\theta = 0^\circ$). Curiously, however, we did observe one transformation in which a $V_2(5-8-5)$ divacancy directly migrated one step in the zigzag lattice direction.

Another interesting observation originating from these simulations is the fact that the displacement threshold for atoms in the central part of the reconstructed defects [$V_2(555-777)$ and $V_2(555-6-777)$] are higher than that for pristine graphene (by as much as 5\%). This may explain why defect structures tend to grow into larger and larger amorphous patches instead of collapsing into holes under continuous electron irradiation at low voltages ($\lesssim 100$ keV).\(^{14}\) Even when atoms are removed from the defect area, the displacements occur at the edges of the existing defects rather than at the central part where the local atomic density is already lower. Clearly, since the core structure of these defects consists of carbon hexagons, there must exist a limiting size above which the displacement threshold becomes similar to that of ideal graphene.

### IV. CONCLUSIONS

To conclude, by combining AC-HRTEM experiments and atomistic simulations, we have shown that the bond rotations which lead to the creation of topological defects in carbon nanostructures are caused by single electron impacts or incomplete annihilation of Frenkel defects. This explains the discrepancy between experimental observations of Stone-Wales defects and their relatively high formation energy and the even higher energy barrier for bond rotation.

The SW transformation in graphene can be initiated in at least two different ways upon electron impact (involving a “circling” or “nudging” motion), and for almost any space angle, provided that enough energy is transferred from the electron to the target atom. Our simulations indicate that SW(55-77) can also appear as a result of “incomplete” recombinaction of a Frenkel defect reminiscent of the formation of Wigner-type defects in silicon.\(^{15}\) However, this is much more likely in the case of local curvature, as in nanotubes. More surprisingly, we also observed sputtering of $C_2$ dimers as a result of annihilation of a Frenkel defect in carbon structures with high curvature.

Moreover, we showed that the displacement threshold of atoms in the central area of reconstructed defects is higher than that of pristine graphene by as much as 5\%, which explains why defective graphene under low-energy electron irradiation ($\lesssim 100$ keV) tends to turn into a two-dimensional amorphous structure\(^{14}\) instead of a perforated membrane. For different divacancy structures, even displacements perpendicular to the graphene layer can initiate SW transformation and thus local structural changes and defect migration.

Our results provide microscopic insight into the irradiation-induced changes in the atomic structure of carbon nanosystems under electron irradiation and, taking into account the interesting electronic properties of defects associated with SW transformations,\(^{14,37,38}\) may open new avenues for irradiation-mediated engineering\(^{19}\) of carbon nanostructures with next-generation electron microscopes.

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Appendix 4

Accurate Measurement of Electron Beam Induced Displacement Cross Sections for Single-Layer Graphene


Accurate Measurement of Electron Beam Induced Displacement Cross Sections for Single-Layer Graphene

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We present an accurate measurement and a quantitative analysis of electron beam induced displacements of carbon atoms in single layer graphene. We directly measure the atomic displacement (“knock on”) cross section by counting the lost atoms as a function of the electron beam energy and applied dose. Further, we separate knock on damage (originating from the collision of the beam electrons with the nucleus of the target atom) from other radiation damage mechanisms (e.g., ionization damage or chemical etching) by the comparison of ordinary (12C) and heavy (13C) graphene. Our analysis shows that a static lattice approximation is not sufficient to describe knock on damage in this material, while a very good agreement between calculated and experimental cross sections is obtained if lattice vibrations are taken into account.

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Radiation damage is one of the key limitations of high resolution transmission electron microscopy (HRTEM) [1]. In particular, the continuous improvements in instrumental resolution [2,3] inevitably entail increased doses per area that need to be applied to a sample. The need for high doses is further increased for new techniques such as single atom or single atomic column spectroscopy [4,7], atomic resolution electron tomography [8], or the analysis of charge distributions from very high signal to noise ratio HRTEM images [9]. For light element materials, such as carbon nanotubes [10,11], fullerenes [12], graphene [13,14], boron nitride [15,16], and probably many more, the dose limitation is particularly severe for three reasons. First, it is obvious, that knock on damage cross sections will be higher for low atomic number elements [17]. Second, the light elements produce less contrast than heavier elements, so that even higher doses are needed to obtain a sufficient signal to noise ratio. And third, most of the novel materials from light elements, such as graphene or carbon nanotubes, appear in the form of low dimensional allotropes that have only one or a few atoms in a typical projection of a high resolution image. While almost all atomic spacings can in principle be resolved by the currently available instrumentation, the question remains whether a sample is stable under the beam until an image has been acquired. In spite of a wide range of previous studies concerning irradiation damage in carbon nanostructures [17–24], a quantitative experimental determination of atomic displacement cross sections for this important class of materials is absent. In fact, only very few quantitative measurements of electron beam induced displacement cross sections [25,26] (beyond damage threshold measurements [27,28]) can be found in the literature. The under standing of irradiation effects is also important for targeted irradiation induced modifications of a material: For the case of graphene, for example, a controlled introduction of vacancies and nonhexagonal rings may lead to derived sp2 hybridized carbon sheets with specific properties [29–34]. Here, we present an extensive measurement and analysis of electron beam induced displacements. We directly count the number of ejected atoms under irradiation as functions of dose, dose rate, and electron energy. Suspended single layer graphene sheets provide the perfect test sample for this analysis: They can be prepared in a precisely defined geometry (1 atomic layer thick, hexagonal lattice, with practically no defects initially), are relatively easy to model, and the number of ejected atoms in multivacancy configurations can be directly obtained from HRTEM images [33,35]. Under 80 keV electron irradiation, the defect free graphene lattice remains undisturbed up to very high doses [9,35] but knock on damage begins already a few keV above this energy [17–24]. Importantly, for energies near the knock on threshold, the changes in the lattice occur slowly, so that the appearance and growth of...
multivacancies can be directly observed in real time. In this way, we can count the number of lost atoms as a function of applied dose and for different acceleration voltages, hence providing a direct measurement of the knock on cross section.

We present insights from a tremendous data set that was obtained for the purpose of quantitating the radiation damage in graphene. We have obtained and analyzed image sequences as shown in Fig. 1 for many acceleration voltage ages (80, 90, 95, 100 kV), and for both, the $^{12}$C “normal”, graphene sample and isotope enriched $^{13}$C “heavy graphene” samples. For all of this data, the defect configurations were analyzed at different doses of exposure, and the number of surviving atoms was counted (see Supplemental Material [36]) for further examples from the data set). We also studied $^{12}$C graphene under 20 keV electron irradiation [37], in order to obtain a further distinction between knock on damage and other effects such as chemical etching or radiolysis. Experimentally, we prepared graphene membranes by mechanical exfoliation and transfer to TEM grids as described previously [38], and by chemical vapor deposition (CVD) followed by transfer to TEM grids, as described in Ref. [39]. We assume that these samples contain the natural isotope composition in carbon, which is 98.9% $^{12}$C and 1.1% $^{13}$C. In addition, we synthesized “heavy graphene” samples made from $^{13}$C, by CVD. The synthesis recipe for the $^{13}$C graphene followed the same procedure as we described in Ref. [39], except that the standard methane precursor was replaced by 99% $^{13}$C enriched methane (purchased from Sigma Aldrich). We aligned an image side aberration corrected FEI Titan 80 300 for HRTEM imaging at 80, 90, 95, and 100 kV, hence providing a closely spaced series around the threshold voltage [20]. The spherical aberration was set to ca. 20 μm and images were recorded at Scherzer defocus. Under these conditions, dark contrast can be directly interpreted in terms of the atomic structure. For 20 kV imaging, we used an image side aberration corrected Zeiss Libra as described in Ref. [37]. In all experiments, long image sequences of the graphene samples were recorded (see videos in the Supplemental Material [36]), typically consisting of ~100 images with 1 s exposures recorded at 2 s intervals and typical dose rates of $10^6$ $^\text{C}_0$/nm$^2$ s$^{-1}$. The sample is under continuous irradiation, only the beam shutter behind the sample is used. We analyze the creation and the increase in the density of vacancies and multivacancies in the image sequences. This approach was feasible up to ca. 100 kV, while at 120 kV the damage occurred too quickly compared to the time or dose needed to acquire an HRTEM image with a sufficient signal to noise ratio.

Example images (for 100 kV, $^{13}$C) are shown in Fig. 1. The left hand side shows images from an image sequence recorded at 100 kV and the right hand side shows the same images with a structure overlay of the atomic configuration. The analysis of such atomic configurations has been described in more detail previously [33,35]: the multivacancies reconstruct into configurations that involve primarily carbon pentagons, heptagons, and octagons as well as other nonhexagonal rings, and can be well assigned from HRTEM data. For counting the atoms, we draw a supercell around the defect clusters, such that the boundary of this cell does not intersect any defect (see Fig. 1). Moreover, the supercell must not contain unpaired dislocation cores, which can be easily verified by counting the number of unit cells on opposing sides of the parallelogram. We then calculate the number of atoms that should be within this cell for the defect free case, and compare it to the number of atoms actually present.

The results of this assessment are shown in Fig. 2, where the number of lost atoms vs total dose per area is shown for all experiments. A linear fit is made for each case, and the slope directly provides the experimental knock on cross section (since a small initial damage may be created before the first image is recorded some of the lines do not go through the origin). Two independent measurements were made for the 100 kV case, but with a 3× different dose rate ($3.5 \times 10^4$ $^\text{C}_0$/nm$^2$ s$^{-1}$ and $1 \times 10^5$ $^\text{C}_0$/nm$^2$ s$^{-1}$). From the nearly identical result, we can exclude a dose rate effect within...
our experimental precision. Under 80 keV irradiation (not shown in Fig. 2), no vacancies were formed in pristine areas up to very high doses (beyond $10^{10} \text{e}/\text{cm}^2$).

We begin our discussion by pointing out the clear difference between the $^{12}\text{C}$ and $^{13}\text{C}$ graphene membranes, and the differences between knock on damage and a chemical etching effect. We find that the generation of vacancies within initially pristine, clean, and defect free graphene membranes depends on the acceleration voltage, and also on the isotope composition ($^{12}\text{C}$ vs $^{13}\text{C}$). Figures 3(a) and 3(b) show graphene membranes of the two isotopes after exposure to 95 keV electrons, where the difference is most clearly visible. Hence, this must be a result of a direct collision between a beam electron and the carbon nucleus: Any chemical effect, or ionization damage, would not distinguish between $^{12}\text{C}$ and $^{13}\text{C}$. As a side remark, we note that graphene membranes made from $^{13}\text{C}$ might provide an even better TEM sample support than ordinary single layer graphene: The contrast background in HRTEM is identical, but the radiation damage rate is lower.

However, in contrast to the vacancy formation, the growth of extended holes in graphene [40] is not predominantly a knock on damage effect: We found that the growth rate of holes in graphene only weakly depends on the electron energy on a wide range of 20 to 100 keV. Holes still form and grow in graphene under 20 keV irradiation [Figs. 1(c) 1(e)], and may even grow faster at low voltages (see Supplemental Material [36]). This is in stark contrast to expectations from knock on damage, where the threshold for displacing edge atoms is expected to be near 50 keV [41]. As shown in Figs. 3(c) and 3(d), the extended holes always nucleate at contamination sites. We noticed that their growth rate is related to the vacuum levels, which varied in the range of $10^{-6}$ to $10^{-2}$ mbar, e.g., with use of the cold trap in the column, the time after insertion of the sample, or different outgassing rates of different sample holders. We conclude that this is beam induced etching with residual water or oxygen in the system as described in Refs. [23,42]. Therefore, we count the formation of vacancies in initially clean and defect free areas as knock on effect, but do not take into account the extended holes that nucleate at contamination sites.

The analysis of our results culminates in the plot shown in Fig. 4. Here, each of the slopes from Fig. 2 provides one data point for a measured displacement cross section. The error bars indicate the statistical variation (standard deviation) in the data. Also shown in Fig. 4 are calculated curves from existing and new calculations that will be discussed below. For two curves, we show a shaded area between $\frac{1}{C^2}$ and $\frac{2}{C^2}$ the calculated cross section, since correlated sputtering of carbon atoms may increase the observed atom loss by up to a factor of 2. After creation of a monovacancy

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**Fig. 2** (color online). Number of displaced atoms vs dose and electron energy. For the 100 keV case, two different dose rates were compared, with (2) having a ca. 3× higher dose rate than (1).

**Fig. 3**. Atomic displacements (knock on damage) vs chemical etching. The comparison between $^{12}\text{C}$ and $^{13}\text{C}$ graphene shows that the formation of vacancies within the pristine lattice is a direct knock on damage effect ($a + b$, $^{12}\text{C}$, and $^{13}\text{C}$ sample after a dose of $1.4 \times 10^9 \text{e}/\text{cm}^2$ at 95 keV). In contrast, the formation of extended holes in graphene is always induced by contamination on the sheet [(c), initial image, and (d) after exposure to ca. $10^3 \text{mbar}$], and the damage rate depends on the vacuum levels. Dashed circles in (c) and (d) denote same areas. (e) Image sequence showing the growth of holes in graphene at 20 keV (example shown for a bilayer area). Scale bars are 2 nm (a) (d) and 5 nm (e).
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Form a stable divacancy (since impacts of energetic energies that are created close to each other may combine and supplement material [36]). In any case, the resulting higher electron energies (this is further discussed in the higher electron energies). In this case, the sputtering rate would not have to be doubled. Qualitatively, one would expect that an atom may effectively double the rate of atom loss [Fig. 4(b)]. As a competing mechanism, two monovacancies may be formed. After creation of a monovacancy, one carbon atom remains with a dangling bond and a much lower emission threshold. Subsequent sputtering of this atom may effectively double the cross section.

by electron impact, one carbon atom is left with a dangling bond and a much lower emission threshold [21,41]. Subsequent (and much more rapid) sputtering of this atom may effectively double the rate of atom loss [Fig. 4(b)]. As a competing mechanism, two monovacancies may be formed. After creation of a monovacancy, one carbon atom remains with a dangling bond and a much lower emission threshold. Subsequent sputtering of this atom may effectively double the cross section.

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FIG. 4 (color online). (a) Measured and calculated knock on displacement cross sections. The lower boundary of the shaded areas correspond to the calculated cross section, while the upper boundary is twice the calculated value (as would be expected for correlated sputtering). The inset shows the calculations for $^{13}$C, 300 K and static lattice on a larger energy range. (b) Correlated displacement of carbon atoms. After creation of a monovacancy, one carbon atom remains with a dangling bond and a much lower emission threshold. Subsequent sputtering of this atom may effectively double the cross section.

adatoms, can not be dominant in our experiment as evidenced by the absence of a dose rate effect. Hence, we expect a rate of atom loss in between 1 and 2 of the value calculated for pristine graphene.

The cross section for Coloumb scattering between an electron and a corresponding target nucleus was derived by Mott [44]. McKinley and Feshbach have found an analytic expression for the Mott scattering cross section as a function of the maximum transferred energy [45],

$$
\sigma_D = \frac{4Z^2 E_e^2}{m_e^2 c^2} \frac{T_{\text{max}}}{T_{\text{thr}}} \pi \alpha \beta \left[ \frac{1}{\beta^2} \right] \left[ 1 + 2 \pi \alpha \beta \sqrt{\frac{T_{\text{thr}}}{T_{\text{max}}}} \right] \ln \left( \frac{T_{\text{max}}}{T_{\text{thr}}} \right)
$$

where $Z$ is the atomic number of the target atoms, $E_e = 13.6$ eV the Rydberg energy, $\alpha_0 = 5.3 \times 10^{-11}$ m the Bohr radius of the hydrogen atom, $\beta = \frac{v}{c}$ (electron velocity $v$, divided by the speed of light $c$), $m_e$ the mass of the electron and $\alpha = \frac{e^2}{\hbar c}$. $T_{\text{max}}$ represents the maximum transferred energy in the collision event and $T_{\text{thr}}$ the threshold energy for atomic displacement. Without modifications, Eq. (1) is suitable to evaluate the total “knock on” cross section for an atom at rest with a given emission threshold energy. The curve from Eq. (1) (“static lattice” in Fig. 4), features a rather sharp onset of radiation damage with increasing acceleration voltage: The cross section is zero up to a well defined threshold (here 108 keV), and then rises to several barn (beyond all our measured values) only a few keV above this threshold. Changing the displacement threshold in the McKinley Feshbach formula predominantly shifts this curve sideways, but does not affect the sharp onset. Hence, independent of the free parameter $T_{\text{thr}}$ this approximation is in clear contrast to our experiment, which shows a smooth onset of the damage cross section between 80 and 100 keV.

Remarkably, our data can be explained by considering the effect of the struck atom’s vibrations on its own displacement. While the effect has been discussed earlier [28,46,47], our measurement provides precise experimental evidence of this intriguing effect. In essence, it means that an atom that is struck by an electron while it happens to move parallel to the electron beam can obtain a higher maximum transferred energy $T_{\text{max}}$ than if it were static. For our calculation, we approximate the phonon distribution of the material in the framework of the Debye model. We use the Debye temperature calculated for out of plane vibrations of $\theta_D = 1287$ K from Ref. [48]. Since $\theta_D$ depends on the speed of sound, it follows for the Debye temperature of $^{13}$C that $\theta_D^{^{13}C} = \sqrt{\frac{2}{3} \theta_D^{^{12}C}}$. We extract the distribution of atom velocities in the beam direction from the model, calculate the maximum transferred energy $T_{\text{max}}(v, E)$ as a function of the atom velocity $v$ and electron energy $E$, and obtain the weighted sum of the sputtering cross section numerically (see Supplemental Material).
In other words, we still use the Mott scattering cross section, but we consider that the atom is not at rest initially. The threshold energy of $T_{th} = 22$ eV was taken from first principles calculations [49] without any adjustments (Refs. [21,22] give similar values). With this value, the smooth onset of knock on damage between 80–100 keV is very well reproduced. For the first time, no adjustment to the calculated threshold energy $T_{th}$ is needed to explain the data, as was the case in previous studies [22,49]. Remarkably, the previous mismatch between theory and experiments was not due to inadequate calculations of $T_{th}$, but because the effects of lattice vibrations on the elastic collision were not considered. Interestingly, the calculated curves are almost identical for the zero Kelvin and room temperature case (Fig. 4, $^{12}\text{C}$ $T = 0$ K and $T = 300$ K curves). This implies that already the zero point energy of the phonon modes is sufficient to explain the increased knock on cross sections as compared to the static lattice.

In summary, we have made an accurate measurement of atomic displacement cross sections for carbon atoms in single layer graphene. The cross section smoothly rises from practically zero (4 barn) at 80 keV to ~0.2 barn at 100 keV. In practice this means that 80 keV imaging of defect free graphene is easily possible, while already 100 keV TEM images might not represent the original configuration of a sample. A static lattice model is not sufficient to model the process, and the contribution of atomic motion adds significantly to knock on damage cross sections near the threshold. The difference between $^{12}\text{C}$ and $^{13}\text{C}$ isotopes is detectable and further confirms the model. While the results on graphene will be important for HRTEM studies of this material and related ones (especially carbon nanotubes), the generalized insights to radiation damage mechanisms should be more generally applicable to any material where knock on damage is important. Our results show that knock on displacement cross sections can be modeled with high accuracy, if lattice vibrations are taken into account.

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Appendix 4


Appendix 5

Atom-by-Atom Observation of Grain Boundary Migration in Graphene

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Adjacent grains in polycrystalline graphene are separated by tilt boundaries. The low-energy configurations of these GBs consist of arrangements of pentagon heptagon (57) pairs with a width below 1 nm, whereas the pristine lattice consists of only hexagonal carbon rings. In contrast to the GBs in most bulk materials, the atomic density in graphene GBs is typically nearly the same as that of the adjacent crystallites (i.e., zero or nearly zero density deficit), likely owing to the strongly covalent bonding between atoms and the energy penalty associated with dangling bonds. The graphene samples used in our study were grown by the chemical vapor deposition technique (Methods) on polycrystalline Cu foils. After growth, the graphene membranes were transferred to commercial TEM grids for electron beam-stimulated modification and simultaneous aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM) imaging in an FEI Titan 80 300 microscope operated at 80 kV (Methods).

An overview of our sample is presented in Figure 1. As can be seen in both the HRTEM image (Figure 1a) and the lower-magnification dark-field image (Figure 1b), the specimen is highly polycrystalline. Even though graphene is known to grow nonpseudotaxially on Cu, the distribution of misorientation angles between adjacent grains (inset, Figure 1a) reveals a strong propensity for neighboring grains to be misoriented by θ ≈ 30°. This is because, in contrast to earlier reports, our sample contains a significant fraction of small grains enclosed within larger ones for which this misorientation is the lowest-energy crystallographic configuration. As expected, the observed GBs are predominantly constructed of continuous chains of (57) pairs and, similar to previous observations, the GBs tend to take on meandering, locally curved configurations. These shapes reduce the lattice strain that would result from straight boundaries separating randomly oriented grains, and which could, in turn, cause buckling of the membrane.

Significant changes in the atomic structure of graphene can be induced via bond rotations under 80 kV electron irradiation, as we have previously shown. Although electron irradiation at 80 kV can displace atoms from edges of holes in graphene, knock-on sputtering of three-coordinated carbon atoms becomes significant only at slightly higher voltages, as is extensively explained in ref 11. Correspondingly, hole growth in graphene under 80 kV electron irradiation is driven by chemical effects, not knock-on displacements. Such irradiation will also...
cause only slight heating of the sample. At voltages below 80 kV, bond rotations are too scarce to lead to significant configurational changes (the lower the voltage, the fewer bond rotations per unit time). Therefore, by exposing graphene to 80 keV electrons, we deliberately maximize the bond rotation rate, resulting in measurable changes in graphene GB morphology during the time scale of a typical experiment in the electron microscope. In the case of straight twin boundaries, the GB energy per unit length ($\gamma$) has already been shown to depend primarily on the misorientation angle ($\theta$). According to our density functional theory (DFT) calculations (Methods), this remains true also for more realistic, serpentine GB configurations ($\theta \approx 30^\circ$ all $\gamma$ are within 0.03 eV/Å, the absolute value being an order of magnitude higher). Therefore, the driving force (per unit GB length) for migration of a given GB between two grains, $\gamma/R$, should depend only on its local in-plane curvature and not on its detailed atomic structure. Hence, at low boundary curvature ($R \rightarrow \infty$) there is no preferred direction of migration, whereas in the high-curvature limit ($R \rightarrow 0$) the driving force should favor decreasing the GB length and thereby shrinking the grain located on the same side of the boundary as the center of curvature. The decrease of GB length in a 2D material is analogous to decrease of GB area in conventional 3D materials.

We first consider the behavior of boundaries between larger grains in the sample. The GB shown in Figure 2 terminates at two holes that formed under the electron beam as a result of electron beam-induced chemical etching occurring at adsorbates attached to the GB outside our area of interest. Such holes grow steadily during a TEM experiment and they might pin the ends of the GB, preventing its migration beyond the pore edges, similar to the Zener-pinning effect in conventional materials. As indicated schematically in Figure 2, the boundary is constructed of a continuous chain of (5/7) pairs interspersed occasionally with distorted hexagons, which similarly serve as dislocation cores in the graphene lattice. The misorientation angle between the grains is close to 30°. As expected, upon continuous irradiation we observe the boundary structure to undergo sequential bond rotations in the series of micrographs recorded during an 11 min exposure (Figure 2a-h). Since the driving force for GB migration is negligible at large $R$, the boundary fluctuates between different shapes around a more-or-less straight configuration, with no favored direction for GB translation. Longer image sequences of such transformations are presented in the Supporting Information Videos 1 and 2.

Next, we direct our attention to smaller grains (~1 2 nm) for which the driving force associated with boundary curvature is expected to become significant. To gain a better understand-
standing of the effect of bond rotations on the energetics and boundary kinetics of small grains, we developed a Metropolis Monte Carlo (MC) code utilizing an analytical interaction model\(^{18}\) (see Methods and Supporting Information for further details). This code allows us to find low-energy transformation routes between different structures connected by a sequence of individual bond rotations. We first created several graphene grains having sizes comparable to those observed experimentally and then studied how bond rotations changed the atomic configurations and total energy at each stage of structural transformation. In Figure 3a,b, we present two examples from our simulations. In both cases, the initial structure rapidly reaches a local equilibrium configuration. However, further reduction in energy takes place only after an energy barrier has been overcome, which requires several bond rotations to occur in sequence, each of which increases the energy of the simulation structure. Under our experimental conditions, such steps can occur only with assistance from the electron beam (the thermal activation rate for bond rotation is extremely low at room temperature, as the required energy is 6 10 eV\(^{19}\)). However, this energy input is more than recovered on the other side of the barrier, thus making the reverse process much less likely.

The simulated atomic configuration presented in Figure 3b eventually transforms into a flowerlike structure.\(^{20,21}\) This hexagon-shaped grain (flower defect) has been reported previously in both nitrogen-doped\(^{20,21}\) and pristine graphene.\(^{22,23}\) Interestingly, a similar structure can form from carbon adsorbates on graphene substrates at high temperatures.\(^{24}\) It is also the single most prevalent grain structure observed in our samples. This particular boundary configuration can be created via six consecutive bond rotations. As noted above, the reverse transformation is unlikely, owing to a considerable energy barrier (circa 8 eV according to the analytical interaction model). Clearly, unlike the reversible changes observed for boundaries with large \(R\), the driving force associated with high-boundary curvature can lead to irreversible shrinkage of smaller grains. The configurational transformations generated by the MC simulations are validated by similar transformations recorded under the electron microscope. One example is shown in Figure 3c (more frames are available in Supporting Information Video 3) and another one in Figure 4d.

When the shrinkage of small grains having zero density deficit is taken to its logical conclusion, one could expect to observe the complete disappearance of these structures. This is indeed possible, as we demonstrate in Figure 4a, which shows
Figure 4. “Unwinding” the flower defect and an example of configurational changes of boundaries with nonzero density deficit. (a) A sequence of micrographs showing the disappearance of a flower defect under an electron flux of approximately $1.0 \times 10^7$ e/($\text{nm}^2\text{s}$) during a 30 s total exposure (micrographs without overlays are presented in Supporting Information Figure 1 and frames with a larger field of view are presented as Supporting Information Video 4). Each intermediate stage of the unwinding process is captured here except for the last one, number 6, the Stone-Wales defect, before pristine graphene is reached. Below the experimental images are DFT-optimized models of the same structures and a plot of their formation energies. Rotating bonds are indicated by black arrows. (b) Evolution of the total energy of an unwinding flower defect in a high-temperature (4000 K) MC simulation. (c) Evolution of the total energy of a similar process in the presence of two other defects (a divacancy and an ad-dimer configuration); in this case, no clear energy barrier is evident. The simulation temperature was 2500 K. (d) Experimental micrographs showing transformations of two grains, one (bottom-left) with nonzero density deficit and another one involving two missing atoms (top) under an electron dose rate of $4.5 \times 10^6$ e/($\text{nm}^2\text{s}$) for a total exposure time of 240 s with schematic presentations of the structures in clean areas underneath each image. (The complete image sequence is presented as Supporting Information Video 5). Scale bars 1 nm.

Although the atomic density in graphene grain boundaries is normally identical to that of the hexagonal carbon lattice, we sometimes observed nonzero density deficit in grains and grain boundaries. In Figure 4c we show an example from our simulations in which an initially larger structure first transforms into the flower defect with a nearby divacancy having the $\text{V}_2(555-777)$ reconstruction and an adatom pair in the $I_2(7557)$ configuration. Here, the two additional atoms at the GB change the energetics of the transformation process, significantly reducing the energy barrier in comparison to the case presented in Figure 4b.

When a GB loop manifests a density deficit, shrinkage of the interior grain is necessarily accompanied by emission of a vacancy structure, as the excess “volume” must be accommodated somewhere in the graphene lattice; experimental evidence for such an event is presented in the upper part of image sequence Figure 4d. In the lower part of the same sequence, we observe how another grain transforms into the flower defect during observation, in striking resemblance to the simulation presented in Figure 3b. In addition, in the lower right corner of the first panel we see a defect structure...
consisting of a (S7) dislocation core and two ad-atoms in the $L_{(555-777)}$ configuration. These ad-atoms vanish between the first and the second panel, showing that such adatom structures are mobile under our experimental conditions, possibly via the bond rotation mechanism (more frames are available in Supporting Information Video 4). In general, due to the experimental time resolution the role of ad-atoms cannot be completely excluded in other transformations. However, since the total number of atoms in the structures remains constant during observation, except in the rare cases discussed above, their role can hardly be a significant one.

In this study, we have demonstrated that GB migration in graphene can be observed atom-by-atom in real time by utilizing AC-HRTEM, which not only provides atomic resolution images, but also stimulates bond rotations that in turn induce changes in GB configurations. As anticipated from macroscopic concepts for the energetics of grain boundary migration, we find that these atomic-scale modifications lead to a time-averaged GB translation only in the presence of significant boundary curvature. Moreover, we show that a single graphene grain fully enclosed within another one can even shrink to the point of disappearance, resulting in the restoration of pristine lattice. These findings suggest that graphene may offer the first experimentally accessible platform for in situ atomic-level investigation of a host of GB phenomena, including solute drag, Zener pinning, interaction with other lattice defects and coupling to mechanical stresses.

**Methods. Sample Preparation.** Single and few-layer graphene films were prepared by vacuum-assisted chemical vapor deposition on polycrystalline Cu foils using hexane as a liquid precursor. The Cu foil was heated to 950 °C in the presence of ≈5 mbar of forming gas, Ar-5% H₂, flowing at a rate of ~400 sccm; the forming gas prevents oxidation of the Cu substrate during annealing. Once the desired temperature was achieved, the Ar/H₂ flow was stopped, and hexane vapor was introduced into the quartz tube under a pressure of 0.5 mbar and a flow rate of ≈4 mL/h, maintaining these conditions for 1 min. Finally, the sample was cooled to room temperature under flowing forming gas at a pressure of ~5 mbar.

**AC-HRTEM Imaging.** Aberration-corrected high-resolution (AC-HR)TEM imaging was carried out in an FEI Titan 80 300 transmission electron microscope equipped with an objective-side image corrector. The microscope was operated at 80 kV. The extraction voltage of the field emission source was set to a reduced value of 2 kV in order to minimize the energy spread of the electron beam. The spherical aberration was set to a reduced value of 2 kV in order to minimize the field emission source. The spherical aberration was set to a reduced value of 2 kV in order to minimize the field emission source.

**Electronic Structure Calculations.** Density functional theory (DFT) calculations were carried out using the VASP simulation package, using projector augmented wave potentials to describe core electrons and the generalized gradient approximation to account for exchange and correlation. The flower defect and divacancy models (see Supporting Information) consisted of 200 atoms. For these particular cases, a kinetic energy cutoff of 500 eV was imposed for the plane waves, and a Monkhorst Pack k-point mesh of $7 \times 7 \times 1$ was employed. Initially created defect configurations were relaxed until atomic forces were below 0.01 eV/Å. The more complex models for estimating the GB energy consisted of 800 atoms. In these cases, the kinetic energy cutoff was set to 1000 eV, and a single $k$-point (Gamma) was used with 0.1 eV/Å as the atomic force convergence criterion in order to reduce the computational expense.

**Metropolis Monte Carlo Method.** We implemented the MC model so that for each iteration one C-C bond is selected randomly within the simulated graphene structure. After rotation of this bond and complete relaxation of the resulting structure with an analytical model for C-C interactions, the energies of the initial ($\Gamma$) and the trial state ($\Gamma'$) are compared. The transition $\Gamma \rightarrow \Gamma'$ is accepted if the following comparison is true

$$\nu \leq \exp \left( \frac{\Delta E}{k_B T} \right)$$

where $\nu \in [0, 1]$ denotes a random number, $\Delta E = E_\Gamma - E_{\Gamma'}$ the energy difference between $\Gamma$ and $\Gamma'$, $k_B$ the Boltzmann constant, and $T$ the simulation temperature. Note that if the energy decreases during the transition ($\Delta E > 0$), the comparison is true, and the trial state is always accepted.

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**Author Contributions**

These authors contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

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Appendix 6

Atomic scale study of the life cycle of a dislocation in graphene from birth to annihilation

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Atomic scale study of the life cycle of a dislocation in graphene from birth to annihilation

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Dislocations, one of the key entities in materials science, govern the properties of any crystalline material. Thus, understanding their life cycle, from creation to annihilation via motion and interaction with other dislocations, point defects and surfaces, is of fundamental importance. Unfortunately, atomic-scale investigations of dislocation evolution in a bulk object are well beyond the spatial and temporal resolution limits of current characterization techniques. Here we overcome the experimental limits by investigating the two-dimensional graphene in an aberration-corrected transmission electron microscope, exploiting the impinging energetic electrons both to image and stimulate atomic-scale morphological changes in the material. The resulting transformations are followed in situ, atom-by-atom, showing the full life cycle of a dislocation from birth to annihilation. Our experiments, combined with atomistic simulations, reveal the evolution of dislocations in two-dimensional systems to be governed by markedly long-ranging out-of-plane buckling.

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The central role of dislocations in determining the behavior of solid state matter has been extensively investigated in materials sciences since the first formulation of the dislocation concept at the beginning of the twentieth century and their experimental discovery 50 years later. However, up until now, atomic scale studies of creation, migration and annihilation of dislocations have been reserved for theory and atomistic simulations, as monitoring changes in the structure of materials with atomic resolution has been well beyond the spatial and temporal limits of experimental characterization techniques. Lower resolution observations of dislocation motion have been made already in the 50’s (ref. 5), using a transmission electron microscope (TEM). TEM has proven to be a powerful tool for studying the structure and arrangement of dislocations, with seminal work laid out by Cockayne et al. in 1969 by the introduction of the weak beam method.

Recently, Hashimoto et al. showed the appearance of a dislocation in sp² hybridized carbon, and Warner et al. presented atomically resolved aberration corrected high resolution TEM (AC HRTEM) images of dislocations in graphene, demonstrating the basic glide and climb steps. In both works, the appearance of the dislocations was attributed to displacement and reorganization of carbon atoms. However, the actual steps in the underlying dynamical process have not yet been observed experimentally at the atomic scale. This is what we report here thanks to the two dimensional (2D) nature of graphene, which facilitates AC HRTEM observations of the structural changes.

The two dimensionality, however, also introduces peculiarities: as there are no neighboring atomic planes inhibiting out of plane deformations, the presence of dislocations with their associated strain fields may lead to strong out of plane corrugations. This can be readily illustrated by considering a plain sheet of paper: try to compress it in the in plane direction or perhaps pinch it in the center, and it will most certainly not get smaller, but will rather buckle. The importance of three dimensional (3D) buckling in strained 2D materials has been pointed out earlier. However, as accounting for 3D out of plane deformations significantly complicates calculations, such deformations have either been omitted in theoretical studies, or the studied systems have been too small to describe the long range corrugations.

In order to follow the whole life cycle of a dislocation atom by atom, we have here employed AC HRTEM using the electron beam both to image the dynamics of atoms in a suspended single layer graphene sheet and to stimulate atomic level structural changes. It is well known that in graphene, high energy electron irradiation can induce sputtering of carbon atoms and bond rotations (so called Stone Wales transformations). In our experiment, we used an operating voltage of 80 kV, which is below the static sputtering threshold in graphene. However, thermal vibrations lead to non zero displacement cross section and therefore allow occasional sputtering. As the structural changes were of specific interest in our experiment, we increased the temporal frequency of the transformation events by working at exceptionally high beam currents (up to 1 x 10⁶ e⁻⁻² s⁻¹, that is, one to two orders of magnitude higher than what is typically used for purely structural investigations). The whole life cycle of an edge dislocation is presented below at atomic resolution, including its creation, motion, interaction with other dislocations and eventual annihilation. The dislocations are first formed by sputtering carbon atoms by the energetic electrons, followed by reorganization of the vacancy agglomerates. The dislocations are seen to migrate either via bond rotations or further sputtering of atoms. A markedly long ranging interaction of the dislocations is observed, and is determined to be mediated by strong out of plane buckling of graphene, rather than in plane strain as assumed previously. Owing to an attractive force acting between the dislocation cores, the cores are driven towards each other, ultimately resulting in the annihilation of the defects. As a whole, these observations comprise the first atomic scale observation of the full life cycle of dislocations in any material.

Results

Birth of dislocations in graphene. When carbon atoms are knocked out from the graphene lattice, vacancy type defects, such as that shown in Fig. 1a are formed. Prolonged irradiation leads to further carbon sputtering, and isolated vacancies agglomerate into larger vacancy structures (see Fig. 1b d). It has been predicted that for > 10 missing atoms it is energetically favorable for the vacancy agglomerate to locally reorganize into a dislocation dipole terminated by two edge dislocations. This is exactly what

Figure 1 | The birth of a dislocation dipole in graphene. Two edge dislocations are created via sputtering of carbon atoms and reorganization of the multi vacancy structure. The upper panels show the original AC HRTEM images with low pass Fourier filtering applied and the lower panels show the same frames with maximum filtering applied for better visibility (see Supplementary Figure S1 for details). In panel a, two atoms have been removed, forming a divacancy. In each subsequent panel b e two more atoms have been removed and the defect has undergone considerable reorganization. In panel e, with ten missing atoms, the defect structure has reorganized into a dislocation dipole with two edge dislocations at its ends pointing away from each other. This birth event is shown in Supplementary Movie 1. The scale bar is 1 nm.
can be observed in Fig. 1e, where the vacancies are rearranged into a missing row of atoms in between the two dislocation cores (see Supplementary Figure S2 for details of the structure). In the following, such dislocations are termed to be pointing away from each other, and dislocations in the opposite orientation are termed to be pointing towards each other. In general, dislocations are created through variations of such a process in our experiment, with a multi vacancy complex preceding the birth of a dislocation dipole.

**Motion of dislocations.** Edge dislocations can migrate in the graphene lattice by climbing and gliding in different directions as schematically shown in Fig. 2. In the climb motion, atoms are either added or removed next to the dislocation core (see Supplementary Figure S3 for details). In practice, under our experimental conditions, removal of atoms happens frequently, while adding new atoms into the lattice is a more rare event. Nevertheless, filling of a divacancy was also observed in our experiment (see Supplementary Figure S4). This leads to climb happening predominantly in the direction shown in the figure (the atoms marked with crosses are removed). We would like to point out that atoms next to the dislocation core are much more frequently sputtered in our experiment, as compared to the intact parts of the lattice. This indicates a lowered displacement threshold for those atoms, which was also validated by our simulations (see Supplementary Figure S5). Simple glide motion is facilitated by a Stone-Wales transformation, where two neighboring carbon atoms (marked with the ellipse in the figure) rotate by 90° around their midpoint, resulting in the movement of the dislocation by 0.25 nm (see Supplementary Figure S6 for details). HRTEM images of these steps are shown in Fig. 2b–e, and have been also presented by Warner et al.9 These basic climb and glide steps are not necessarily typical for the dislocations, however, as migration tends to take more complex forms, such as that displayed in Fig. 2f–h. Here, the dislocation first transforms via a bond rotation into a chain of dislocations (dubbed a ‘dislocation worm’ elsewhere13), which has earlier been predicted to have a lower formation energy under strained conditions. Subsequently, another bond rotation moves the dislocation two glide steps (0.5 nm) away from the original site. Even more complex migration processes can be seen underway in the upper right corners of Fig. 2d and e and in Supplementary Movie 2.

**Interaction of dislocations.** In order to predict the effect of the removal of the string of atoms on the structure of graphene, we conducted conjugate gradient structural relaxations of a large graphene supercell (∼25 × 25 nm and ∼24,000 atoms) containing a dislocation dipole in various configurations, employing an analytical force field26 to describe the C-C interactions. The missing string of atoms induces tensile strain in between the dislocation cores and compression outside this area11. However, as the stress required to stretch the surrounding exceedingly large graphene sheet is very small and the compressional strain can be released via out of plane corrugations (the energy constants characterizing in plane and compressional strain can be released via out of plane corrugations (the energy constants characterizing in plane and flexural stiffness differ by two orders of magnitude27), the width of the system was set to such a value that strain across the dislocation dipole is zero and the graphene sheet was allowed to buckle. Counter intuitively, the damaged parts where the atoms were removed stay close to the pristine state, whereas the rest of the sheet is buckled, with slowly fading out of plane deformations extending over large distances. However, if the corrugations of two dislocation cores pointing towards each other (that is, originating from different dipoles) overlap, they can terminate each other. Examples of such situations are depicted in Fig. 3c and d.

To study how this affects the energetics of the system, the potential energy of the system was mapped as a function of glide and climb distance of the cores. The resulting energy landscape is shown in Fig. 3a, with each point normalized to the number of atoms. Towards the lower left corner, the dislocations come closer to each other. Going up in the map means increasing the climb distance and the number of atoms, whereas going right increases the glide distance. As bond rotations happen much more frequently than sputtering, dislocations can easily migrate towards an energy minimum in the horizontal direction for any given vertical climb distance.

The general trend in the energy map is clear: the closer the dislocations come, the lower the energy becomes, resulting in an attractive force acting between the dislocations over large distances. The cores now effectively form a dislocation dipole with a row of extra atoms in between them. The buckling can take place in different modes, depending on whether the individual dislocations are extended out of the plane in the same or opposite directions. These modes are presented in Fig. 3c and d, where the symmetrical extension is named the S mode, and anti symmetrical one the AS mode.
The energetics change depending on which mode is taking place, which can be seen in Fig. 3b, where the energy is plotted at a fixed climb distance of 1.7 nm. The system finds its global energy minimum in the S mode at zero glide distance, and the energy in this mode increases monotonously with increasing glide distance. The AS mode has a significantly higher energy at small glide distances, but as the distance increases, the energy goes down, and the mode becomes energetically favorable after a certain crossing point, the location of which depends on the climb distance. The AS mode has an energy minimum at a location that depends on the climb distance (1.2 nm for the presented case), after which the system starts to increase, leading to an attractive force also in this mode. As is shown later, in the experiment, the dislocations tend to reside exactly at the distance where the energy minimum is predicted to be.

The calculated significant out of plane buckling was confirmed by our experiments. Traditionally, TEM is considered to be insensitive to 3D features of a sample, due to the inherently wide depth of focus of the instrument. However, in an AC HRTEM image, the brightness of the center of a carbon polygon is sensitive to its projected size. This means that if a polygon is tilted, for example, due to a corrugation, its center becomes less bright. Compared to the lattice contrast, these variations are small, and hence they are not clearly visible without image processing (see Fig. 4a). However, by applying maximum filtering on the digital images, where the brightest pixels are expanded to cover their neighborhood up to a predefined radius, the variations in the polygon brightnesses can be amplified (see Supplementary Figure S1 for details). Similar information can be extracted using geometrical phase analysis, as was demonstrated recently by Ortolani et al.28. However, the interpretation of geometrical phase analysis results is biased towards reading the apparent reduction in bond lengths as compression rather than tilting, as in a previous study9, where as high as 27% compression of bonds was reported next to the dislocation cores.

Figure 3 depicts the energies of the two different buckling modes as a function of glide distance at a fixed climb distance of 1.7 nm. Panels a and d visualize different buckling modes, which depend on whether the dislocations extend out of the plane symmetrically (S mode) or anti-symmetrically (AS mode). Red color indicates elevation and blue depression in the positions of the carbon atoms. On the left side of the solid line in panel a the S mode is energetically favorable, and the AS mode is favorable to the right of the line. The horizontal dotted line indicates the climb distance corresponding to the data presented in panel b.

Figure 4a shows an AC HRTEM micrograph of two interacting dislocation cores. Panel b presents the same image after processing. A clearly visible dark ridge connecting the dislocation cores is observable, indicating a reduced projected size of the polygons along that line. This can be attributed either to corrugations or compressive strain, as both of them reduce the projected size of the polygons.

To identify which scenario takes place in the experiment, the same dislocation configuration was relaxed first by allowing the structure to buckle and next by constraining the geometry to be flat. The first relaxation resulted in the corrugated structure visualized in Fig. 4d. The structure was subsequently used for HR TEM image simulation. Applying identical filtering as was used for the experimental image resulted in strikingly similar features as compared with the experiment.

The total energy of the flat relaxed system is 17 eV higher than in the previous buckled case. Further on, its simulated and filtered image (Fig. 4g) proved to be in disagreement with the experimental one. Most importantly, the dark ridge connecting the dislocations is absent. Similar simulated image to Fig. 4e would result from a flat atomic structure with the same in plane coordinates as in the buckled structure. The total energy of such a configuration ends up 145 eV higher in our simulation. Thus, the contrast observed in the experimental image is likely due to out of plane buckling of the graphene sheet rather than bond contraction, and the corrugations in the experiment follow the prediction of the simulations.

The markedly long range nature of the corrugation mediated interactions of dislocations and other defects can be observed in Fig. 4c. The dark ridge extends over the length of 7 nm terminating at separate defects. More examples with even longer ranges are presented in Supplementary Figure S7 and Supplementary Movie 3. One can further conclude that even at fairly low concentrations, point defects in graphene can no longer be considered isolated. Instead they form an interconnected
network, as the strain fields or ‘corrugation fields’ of interacting defects strongly affect the energetics of the system.

Annihilation of dislocations. As edge dislocations in graphene pointing towards each other have net attraction, and both the glide and climb mechanisms are activated by the electron beam, dislocations should migrate towards each other and undergo annihilation. This is precisely what we observed experimentally. In Fig. 5a, four dislocations are present. The dark ridges, indicating the interlocking of the corrugations of the dislocations, are visible in the filtered images. The left most dislocations approach each other, following the previously predicted path of local energy minima. Finally, they disappear, leaving a perfect hexagonal graphene lattice behind. At close proximity, a larger reorganization takes place (panel d). This reconstruction resembles the intermediate configurations in Fig. 1, but actually has extra atoms instead of vacancies, consisting of two adatom pairs and a Stone Wales defect.

The right most dislocation pair also causes reorganization of the lattice in between them. In this case, however, the reorganization leads to the formation of a small closed grain boundary loop (the flower defect). They have been reported to form under an electron beam29 and have been demonstrated to be highly stable30. While the dislocations undergo annihilation and the atomic density becomes equal to the pristine lattice, the small grain is left behind. This sequence can be seen in Supplementary Movie 5 and 6.

Discussion
The whole life cycle of an edge dislocation in graphene, including its creation, motion, interaction with other dislocations, and finally annihilation was presented atom by atom and step by step using an aberration corrected high resolution electron microscope for both imaging and inducing transformations in the atomic structure. The dislocations were created by sputtering carbon atoms due to impacts of energetic electrons, and subsequent reorganization of the graphene lattice. The dislocations were seen to migrate through the bond rotation mediated glide mechanism, as well as the climb mechanism facilitated by removal of carbon atoms. A markedly long ranging interaction of the dislocations was observed. The interaction is driven by strong out of plane buckling of graphene, instead of the previously assumed in plane strain, as corroborated by atomistic computer simulations, as well as image filtering techniques applied to the experimental micrographs. An attractive force acting between dislocation cores was seen to drive the cores towards each other, ultimately resulting in the annihilation of the defects, leaving behind defect free graphene. To our knowledge, this is the first atomic scale observation of the full life cycle of a dislocation—a concept of pivotal importance in materials science.

Methods
Experimental. HR-TEM experiments were carried out in a Cs-corrected FEI Titan 80–300 microscope at an operation voltage of 80 kV. In order to reduce the energy...
Figure 5 | Attraction and annihilation of dislocations in graphene. Panel a has four dislocations. The two left most dislocations inter-act through the AS mode and the right most through S mode. In the subsequent panels b and c the left most dislocations migrate towards each other, making a more complex rearrangement in panel d before undergoing annihilation (panel e), leaving behind defect free graphene. The right most dislocations cause a reorganization of the lattice along the connecting corrugation, resulting in a closed grain boundary loop (also called the flower defect). The dislocations themselves disappear, and the density of the sheet returns to the pristine value, but the grain boundary loop is left behind. Here, white and black circles are overlaid on the pentagons and heptagons to further improve the visibility of the structures. The scale bar is 1 m.

Computational. The atomic structure of graphene with dislocations was studied by carrying out structural relaxations of a graphene sheet with a size of ~25 × 25 nm and consisting of ~24,000 carbon atoms, exact number depending on the dislocation separation. The interatomic forces were described by an analytical bond-order potential. In the calculations, always two oppositely oriented dislocation cores were placed with different glide and climb distances, and the resulting structures were related using the conjugate gradient algorithm as implemented in the in-house code Relax. Similar approach has earlier been applied to modeling strained carbon systems. In the displacement threshold calculation, the interatomic forces were described via the density functional-based tight binding formalism. In these molecular dynamics simulations, the atom of interest was assigned momentum in the normal direction relative to the graphene sheet and after the simulation time of 300 fs, it was determined whether the atom was detached from rest of the structure. The binary search algorithm was used to pinpoint the threshold energy. The simulated system consisted of 152 carbon atoms, with two dislocations separated by five climb steps at zero glide distance. A single k-point was used for the calculations and the simulation was run at 0 K. The HR-TEM image simulations were conducted using the QSTEM software using the multislice algorithm. In the simulations, spherical aberration coefficient of 2 μm, focal spread of 7 nm and Scherzer focus were used.

References

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Author contributions
S.K. planned and executed the TEM experiments under the supervision of U.K. O.L. planned and conducted the theoretical calculations under the supervision of A.V.K., and analyzed the data with assistance from all the authors. All the authors contributed in writing the manuscript.

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Appendix 7

Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation: Defect Production and Doping


Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation: Defect Production and Doping

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Using first principles atomistic simulations, we study the response of atomically thin layers of transition metal dichalcogenides (TMDs) to electron irradiation. We calculate displacement threshold energies for atoms in 21 different compounds and estimate the corresponding electron energies required to produce defects. For a representative structure of MoS$_2$, we carry out high resolution transmission electron microscopy experiments and validate our theoretical predictions via observations of vacancy formation under exposure to an 80 keV electron beam. We further show that TMDs can be doped by filling the vacancies created by the electron beam with impurity atoms. Thereby, our results not only shed light on the radiation response of a system with reduced dimensionality, but also suggest new ways for engineering the electronic structure of TMDs.

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Isolation of a single sheet of graphene in 2004 [1] indicated that strictly two dimensional (2D) materials can exist at finite temperatures. Indeed, inorganic 2D systems such as individual hexagonal BN and transition metal dichalcogenide (TMD) layers were later manufactured by mechanical [2,3] and chemical [4,5] exfoliation of their layered bulk counterparts, as well as by chemical vapor deposition [6,7]. Recently, TMDs with a common structural formula MeX$_2$, where Me stands for transition metals (Mo, W, Ti, etc.) and X for chalcogens (S, Se, Te), have received considerable attention. These 2D materials are expected to have electronic properties varying from metals to wide gap semiconductors, similar to their bulk counterparts [8,9], and excellent mechanical characteristics [10]. The monolayer TMD materials have already shown a good potential in nanoelectronic [3,11,12] and photonic [4,13,14] applications.

Characterization of the h BN [15-17] and TMD [5,6,18] samples has extensively been carried out using high resolution transmission electron microscopy (HR TEM). During imaging, however, energetic electrons in the TEM can give rise to production of defects due to ballistic displacements of atoms from the sample and beam stimulated chemical etching [19], as studies on h BN membranes also indicate [15 17,20].

Contrary to h BN, very little is known about the effects of electron irradiation on TMDs. So far, atomic defects have been observed via HR TEM in WS$_2$ nanoribbons encapsulated inside carbon nanotubes at electron acceleration voltage of 60 kV [21] as well as at the edges of MoS$_2$ clusters under 80 kV irradiation [22], while no significant damage or amorphization was reported for MoS$_2$ sheets at 200 kV [18] a surprising result taking into account the relatively low atomic mass of the S atom. Clearly, precise microscopic knowledge of defect production in TMDs under electron irradiation is highly desirable for assessing the effects of the beam on the samples. This knowledge would allow designing experimental conditions required to minimize damage, as well as developing beam mediated post-synthesis doping techniques. Moreover, information on the displacement thresholds is important in the context of fundamental aspects of the interaction of beams of energetic particles with solids, as the reduced dimensionality may give rise to an irradiation response different from that in the bulk counterparts of the 2D material [23].

Here, by employing first principles simulations, we study the behavior of a representative number of TMDs (21 compounds) under electron irradiation, and calculate the threshold energies for atomic displacements in each system, as well as displacement cross sections as functions of electron beam energy. In the case of MoS$_2$, we also carry out HR TEM experiments and provide evidence of electron irradiation induced production of vacancies in this material. In addition, inspired by the recent advances in introducing impurities in h BN monolayers [24,25] we discuss irradiation mediated doping of TMD materials.

For all calculations in this work, we rely on the density functional theory (DFT) with the Perdew Burke Ernzerhof (PBE) exchange correlation functional [26] and the projector augmented wave formalism as implemented in the simulation package VASP [27,28]. In order to obtain a
comprehensive picture of the irradiation response of TMDs, we consider a large set of layered TMDs: MoX₂, WX₂, NbX₂, TaX₂, PtX₂, TiX₂, and VX₂ (where X = S, Se, or Te), which have similar crystal structures.

We started our study by calculating the displacement threshold energy $T_d$ (the minimum initial kinetic energy of the recoil atom) for sputtering an atom from the material. As in our previous simulations for graphene [29] and BN [20] monolayers, an initial velocity was assigned to the recoil atom (corresponding to instantaneous momentum transfer from the electron to the atom during the impact), then DFT molecular dynamics was used to model the time evolution of the system. In practice, the initial kinetic energy of the recoil atom was increased until it was high enough for the atom to be displaced from its lattice site without an immediate recombination with the resulting vacancy. The calculations were carried out using a 5 × 5 supercell of a MeX₂ monolayer. Test simulations for larger systems gave essentially the same results. The atomic structure of a MoS₂ layer and the simulation setup are shown in Fig. 1(a).

$T_d$ required for displacing a chalcogen atom from the bottom layer of the sheet [cf. Fig. 1(a)] is presented in Fig. 2. In addition to the prototypical MoX₂ and WX₂, we also present results for TiS₂ and TiTe₂. As evident from the figure, $T_d \in [5, 7]$ eV for all studied compounds.

We also calculated the vacancy formation energies ($E_f$) for each of the compounds to see how they correlate with $T_d$. We defined $E_f$ as

$$E_f = E_{\text{vac}} - E_{\text{bulk}} (\mu_X).$$

(1)

where $E_{\text{bulk}}$ and $E_{\text{vac}}$ are the energies of the pristine and vacancy containing supercells, respectively. The chemical potential $\mu_X$ of the chalcogen species is taken as the energy of the isolated atom to enable a straightforward comparison with the results of dynamical simulations. $E_f$, with and without relaxation of the atomic structure of the layer, is also presented in Fig. 2.

In the nonrelaxed case, the energetics is very similar for all materials, and as can readily be noticed the agreement between $T_d$ and the nonrelaxed $E_f$ is striking. This is because during the sputtering of chalcogen atoms from the outermost layer, little energy is transmitted to the surrounding metal atoms due to the sufficiently fast sputtering event and the rigidity of the structure. The energies for the relaxed configurations show a more intriguing behavior. Atomic relaxation for some systems evidently gives rise to a considerable drop in $E_f$, so that the similarity to $T_d$ is lost. This drop quantifies the degree of structural relaxation around the vacancy, which is minor for MoS₂; see Fig. 1(b). The analysis of the electronic structure revealed an occupied bonding type vacancy state close to the valence band maximum and an empty antibonding type state in the mid gap, which stabilizes the structure. For the occupied bonding defect state, the electronic charge is localized at the vacancy site, analogous to bulk MoS₂, where Mo atoms donate electrons to S atoms. This is true for all of the semiconducting materials: MoX₂, WX₂, and PtX₂. The rest of the considered materials are metals or semimetals, for which the bonding vacancy state may become unoccupied, which is reflected in larger relaxation and lower formation energies.

Knowing $T_d$, it is possible to estimate the electron threshold energy through the relativistic binary collision formula and the atom displacement cross section (for relatively light atoms) by using the McKinley Feshbach formalism [30]. $E_f$ for Se and Te compounds is smaller than in S compounds, but due to the higher atomic mass their creation through ballistic electron impacts requires significantly higher electron energies. In the case of MoS₂, MoSe₂, and MoTe₂, $T_d$ of 6.9, 6.4, and 5.9 eV correspond to electron energies of about 90, 190, and 270 keV, as calculated assuming a static lattice. For other compounds, the required electron energies...
should be of similar magnitude, based on the close values of $T_d$ in Fig. 2. An accurate estimation of the displacement cross section requires including the effects of lattice vibrations on the energy transferred from an electron to a target atom [31]. We calculated the cross sections for vacancy production as a function of electron energy for MoS$_2$, WS$_2$, and TiS$_2$ beyond the static lattice approximation, as shown in Fig. 3. We stress that the production of S vacancies for practically all TMDs is within the energies commonly used in TEM studies.

The displacement thresholds for chalcogen atoms in the (top) layer facing the beam proved to be considerably higher than for the bottom chalcogen layer, as the displaced atom is “stopped” by the other layers. However, after a vacancy is created in the bottom layer, the threshold energy for the top layer facing the beam proved to be considerably higher for practically all TMDs is within the energies commonly shown in Fig. 3. We stress that the production of S vacancies for practically all TMDs is within the energies commonly used in TEM studies.

The displacement thresholds for chalcogen atoms in the (top) layer facing the beam proved to be considerably higher than for the bottom chalcogen layer, as the displaced atom is “stopped” by the other layers. However, after a vacancy is created in the bottom layer, the threshold energy for the top S atom in MoS$_2$ to be displaced and fill the vacancy is about 8.1 eV. This is similar in magnitude to the threshold for displacing S atom from the bottom layer (6.9 eV), and thus formation of vacancy columns should be possible even at 80 kV when lattice vibrations are accounted for. $T_d$ for transition metals is even higher, since they are bonded to the S sublattice is quickly destroyed. Formation of transition metal vacancies is thus considered highly unlikely.

With regard to possible vacancy agglomeration under continuous irradiation, we found that creation of a vacancy does not alter the formation energy in the neighboring sites in the semiconducting TMDs. Thus, we do not expect accelerated formation of large vacancy clusters. In the same vein, however, it is worth noting that chalcogen atoms may also be sputtered fairly easily from the edges of nanostructures [21,22]. For example, our calculations for a WS$_2$ ribbon show that the chalcogen atoms at the edge can have a displacement threshold as low as 4.2 eV, as compared to 7.0 eV away from the edge.

To check our theoretical results on irradiation induced vacancy formation in MoS$_2$, we experimentally studied the evolution of a MoS$_2$ sheet under an 80 keV electron beam. First, freestanding single layer MoS$_2$ samples were prepared by mechanical exfoliation of natural MoS$_2$ bulk crystals, followed by characterization via optical microscopy on a Si + 90 nm SiO$_2$ substrate and transfer to a perforated TEM support film (Quantifoil), similar to graphene samples [32]. The TEM grid was adhered to the SiO$_2$ surface by evaporating isopropanol on top of it. After this, the silica was etched with KOH. Aberration corrected (AC) HR TEM imaging was carried out in an image side Cs corrected FEI TITAN microscope at a primary beam energy of 80 keV. The contrast difference between the Mo and S sublattice is clearly detectable in the AC HR TEM images proving the single layer nature of the sheet (for a double layer, the contrast would be identical as Mo is stacked above S). This is also confirmed in diffraction measurements, as successive diffraction spots from one (hk0) family show different intensity, whereas for bi and multilayers they are equal [18]. The analyzed intensity ratio of the [1100] diffraction spots was found to be 1.07.

During continuous imaging we found an increasing number of vacancy sites (exclusively on the S sublattice) accompanied by crack formation [see Fig. 4(a)] and lateral shrinkage of the membrane. Counting the actual number of sputtered atoms as in Ref. [31], the cross section for sputtering was found to be 1.8 b, which is in a reasonable agreement with the calculated cross section of 0.8 b, taking into account that the theoretical estimates are very sensitive to inaccuracies in the parameters of the model (e.g., $T_d$ and the velocity distribution) at energies below the static threshold.

In Figs. 4(d) and 4(e) we present simulated TEM images [33] for the single and double vacancies, respectively, based on atomic structures [Figs. 4(b) and 4(c)] obtained from the DFT calculations. Similar defects are observed in the experimental TEM images [Fig. 4(f)]. Different defects can clearly be distinguished by analyzing the (Michelson) contrast relative to the contrast of the Mo atoms in the pristine area. We find that the experimental (simulated) ratios are 0.9 (0.9) for a sulfur column, 0.5 (0.4) for the single and 0.2 (0.2) for the double vacancy.

Having shown that vacancies can be created in TMDs under electron irradiation, we move on to study whether they could be consecutively filled with other atomic species deliberately introduced into the TEM chamber. We calculate the formation energy of substitutional defects in MoS$_2$ and consider donors F, Cl, Br, and I; acceptors, N, P, As, and Sb; double acceptors C and Si; hydrogen H and H$_2$;
and isoelectronic species O, S, Se, and Te. The formation energies and the local density of states (LDOS) around the substitution site are shown in Fig. 5. We list the formation energies with three different chemical potentials of the substituted (impurity) species: the isolated atoms, diatomic molecules, or molecules with hydrogen (CH₄, SiH₄, NH₃, PH₃, AsH₃, HF, HCl, and HBr), where we set $\mu_H = \frac{1}{2} E_H$.

Because of the high formation energy of the vacancy, all substitutions are energetically favored with respect to the isolated atom. However, with respect to $\mu$ in the molecule, C, Si, and N substitutions have positive formation energies. Obviously, even if the equilibrium energetics does not favor the formation of the substitutional defect, the substitution may still be achieved under an electron beam, because molecules like N₂ or hydrocarbons will constantly break apart under the electron beam, and possibly due to electrical charging of the sample [34]. Thus postsynthesis electron mediated doping may also be realized in 2D TMDs, similar to BN sheets [24,25]. The LDOS shows that N, P, As, and Sb behave as acceptors, whereas F, Cl, Br, and I are likely to be donors. C and Si have levels in the middle of the gap and the isoelectronic species like O, Se, or Te do not produce any localized states, as expected.

Filling of the vacancies was also observed in the TEM images, as shown in the series of panels in Figs. 5(c) 5(e). Although we could not identify the type of the impurity, this example proves that electron beam mediated doping is possible. Consequently, through control of atomic species in the TEM chamber and the choice of the electron energy, modification of the physical properties of TMDs via electron beam should be attainable.

To conclude, we calculated atom displacement threshold energies in a number of TMDs. These energies are a measure of the radiation hardness of the material, and serve as critical input parameters in the Kinchin Pease and other semiclassical theories of defect production and ion stopping [23,35]. Here we use them to calculate electron displacement energies and corresponding sputtering cross sections to quantitatively assess the amount of damage created in 2D TMD materials during a TEM experiment via knock on processes. Observations of vacancies in our experimental AC HR TEM images of single MoS₂ sheets validate our theoretical predictions. Finally, we observe filling of the vacancies and discuss the prospects for electron beam mediated doping of TMDs.

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Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation


Appendix 8

From point to extended defects in two-dimensional MoS$_2$: Evolution of the atomic structure under electron irradiation


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From point to extended defects in two-dimensional MoS$_2$: Evolution of atomic structure under electron irradiation

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By combining high-resolution transmission electron microscopy experiments and first-principles calculations, we study production, diffusion, and agglomeration of sulfur vacancies in monolayer MoS$_2$ under electron irradiation. Single vacancies are found to be mobile under the electron beam and tend to agglomerate into lines. Different kinds of such extended defects are identified in the experiments, and their atomic structures and electronic properties are determined with the help of calculations. The orientation of line defects is found to be sensitive to mechanical strain. Our calculations also indicate that the electronic properties of the extended defects can be tuned by filling vacancy lines with other atomic species, thereby suggesting a way for strain and electron-beam-assisted engineering of MoS$_2$-based nanostructures.

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I. INTRODUCTION

Inorganic two-dimensional (2D) transition metal dichalcogenide (TMD) monolayers have recently been manufactured by mechanical \cite{1,2} and chemical \cite{3,4} exfoliation of their layered bulk counterparts, as well as by chemical vapor deposition. \cite{5,6}
The TMDs have a common structural formula $\text{M}_n\text{X}_2$, where $\text{M}$ stands for transition metals (Mo, W, Ti, etc.) and $\text{X}$ for chalcogens (S, Se, Te). \cite{8,9}
The prototypical TMD material is MoS$_2$, \cite{10,11} which is a semiconductor with an optical band gap of about 2 eV \cite{12,13}. It can be doped n or p type, \cite{14} and shows fairly high carrier mobilities, \cite{15} excellent mechanical characteristics, \cite{16,17} and intriguing optical properties. \cite{18,19}
These properties may find use in logical devices, \cite{20,21} flexible electronics, \cite{22,23}
phonotronics, \cite{24,25,26} and gas sensing. \cite{27,28}

High-resolution transmission electron microscopy (HR-TEM) has been used in numerous studies to characterize 2D materials with atomic resolution. This technique has also been applied to various TMDs, \cite{29,30,31,32} and shows fairly high carrier mobilities, \cite{33,34} excellent mechanical characteristics, \cite{35,36} and intriguing optical properties. \cite{37,38} These properties may find use in logical devices, \cite{39,40} flexible electronics, \cite{41,42}
phonotronics, \cite{43,44,45} and gas sensing. \cite{46,47}

II. METHODS

Free standing monolayer MoS$_2$ samples (note that the monolayer consists of three atomic layers) were prepared by mechanical exfoliation of natural MoS$_2$ bulk crystals, followed by characterization via optical microscopy on a Si+90 nm SiO$_2$ substrate and transfer to a perforated TEM support film (Quantifoil), as described in Ref. 33. Aberration-corrected AC-HRTEM imaging was carried out at room temperature in an image-side Cs corrected FEI TITAN microscope operated at a primary beam energy of 80 keV, a current density of $\sim 1.3 \times 10^3$ e/nm$^2$/s, and single frame acquisition time of 1 s. The contrast difference between the Mo and S sublattice is clearly detectable in the AC-HRTEM images proving the monolayer nature of the sheet (for a bilayer the contrast would be identical as Mo is stacked above S). This is also confirmed in diffraction measurements, as successive diffraction spots from one \{hkl\} family show different intensity, whereas for \{hkl\} multilayers, they are equal. \cite{1}
The analyzed intensity ratio of the \{1100\} diffraction spots was found to be 1.07.

Our first-principles calculations were carried out within the framework of the density-functional theory (DFT) implemented in the VASP package based on plane-wave basis and the projector augmented wave formalism. \cite{48,49} Electron-electron interactions were treated using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. \cite{50} As we here only consider defects within single layer MoS$_2$ sheets, PBE is expected to provide good description of the local properties, without the need for dispersion-corrected (van der Waals) functionals. In order to accommodate the long-range strain fields of the defect structures within the computational cell,
we use a relatively large rectangular $10 \times 8\sqrt{3}$ supercell of MoS$_2$. Migration paths are calculated using the nudged elastic band (NEB) method. The relative formation energy $E_f$ of vacancy agglomerates is given with respect to the same number $N_{\text{vac}}$ of isolated vacancies:

$$E_f(N_{\text{vac}}) = E_{\text{tot}}(N_{\text{vac}}) - N_{\text{vac}} E_{\text{tot}}(SV),$$

(1)

where $E_{\text{tot}}(N_{\text{vac}})$ and $E_{\text{tot}}(SV)$ are the total energy of supercells containing $N_{\text{vac}}$ vacancies and a single vacancy, respectively. The relative formation energy of an isolated vacancy is then zero by definition. Negative values of $E_f$ point towards the tendency of vacancies to agglomerate, while positive values indicate that such configurations are energetically unfavorable.

### III. RESULTS

#### A. Line formation under electron irradiation in a TEM

The initial AC-HRTEM image of the sample is shown in Fig. 1(a). It contains a number of vacancies, which may have already appeared due to the TEM-grid transfer procedure. On the other hand, vacancies and substitutional impurities could have been present in the starting material (with any light elements rapidly sputtered from the sample). During imaging, new vacancies are continuously produced, as was already reported in Ref. 33. The vacancies are also seen to diffuse, although at a fairly slow rate, to be discussed in more detail in Sec. III C.

With increasing vacancy concentration, defect agglomeration is expected. Here, formation of extended line defects is observed instead of, e.g., triangular vacancy clusters. The atomic structure of these lines appear to be well described by a row of single vacancies [cf. SV in Fig. 1(d)], without significant atomic reconstruction. However, the tendency to line up and to remain as a line is not very strong, suggesting that the energy gain is small.

After prolonged exposure to the electron beam, and further increase in vacancy concentration, the nature of the lines changes. The lines become wider, where, in essence, the lines extend to span two neighboring rows of the S sublattice. Figures 1(b) and 1(c) show two sequential images of the formation of this kind of vacancy lines. During the formation, the number of single vacancies surrounding the line has dropped significantly, suggesting that the line is formed through agglomeration of these vacancies rather than through production of a large number of new vacancies. The positions of the vacancies far from the line defect remain the same. Furthermore, the atomic structure has undergone significant changes as compared to the single vacancy line.

#### B. Determination of the atomic structure of line defects

Representative experimental images of the two types of vacancy lines, from here on denoted as single vacancy (SV) and double vacancy (DV) lines, are shown in Figs. 2(a) and 2(d). In order to determine the underlying atomic structure, we performed first-principles calculations for various atomic models corresponding to vacancy lines. The optimized geometries [shown in Figs. 2(b), 2(e), 2(g), and 2(i)]—note that the bottom views are given in panels (b), (e), (g), and (i)] are used as an input for TEM image simulation [see Figs. 2(c), 2(f), 2(h), and 2(j)], which are then compared to the experimental images. The images were simulated using Cs of 0.02 nm and the corresponding Scherzer focus of $-11.2$ nm. The relative formation energies for these structures are given in Fig. 2(k).
In the case of SV lines, there is only one reasonable choice for the underlying atomic structure, and the simulated and experimental images agree well. The formation energies show that agglomeration to a line leads to energy gain of about 0.05–0.2 eV per S vacancy, agreeing well with the tendency to line up.

A typical experimental image for a line of double vacancies (DV) is shown in Fig. 2(d). The structure has reconstructed, and several possible atomic structures can be envisioned. The three models attempted here are shown in Figs. 2(e), 2(g), and 2(i), and correspond to (1) two neighboring lines of S vacancies at the same side of the MoS$_2$, (2) Two lines of vacancies at the opposite sides of MoS$_2$ thereby forming a line of vacancy columns (subsequently showing Mo-Mo bonds with bond length close to that in bulk Mo). (3) Two lines of vacancies are at the neighboring sites and opposite sides in “staggered” configuration. From the comparison of the simulated and experimental TEM images, it is clear that the agreement is good only for the staggered model. In addition to the general features of the images, we also found agreement in the lattice contraction perpendicular to the line, as indicated by the ratios of line segments (the red lines in Fig. 2).

Furthermore, the only model yielding negative formation energies is the staggered one. Equal number of vacancies on both sides of the monolayer leads to minimal bending of the sample and thereby promotes lower formation energies. When the length of the line exceeds four units ($N_{\text{vac}} > 8$), this kind of vacancy lines become energetically favored over the SV lines. Therefore the DV line in experiments is assigned to this structure (model 3).

For all the line structures discussed above, vacancies along the line were always on the same side of the monolayer. This is due to the fact that the formation energies tend to increase whenever the vacancies are on different sides of the sheet, but in the same line. For example, the formation energy of an SV line of length 4 with all vacancies on the same side showed 0.7 eV lower formation energy as compared to a case with the vacancies placed in an up-down-up-down configuration. We
stress that vacancy formation should occur predominantly on
the bottom layer, but it is not possible to distinguish between
top and bottom S vacancies in our AC-HRTEM setup.

We note that the atomic structures of these lines are
different from those found in Refs. 49 and 50. Whereas our
lines are produced by the electron irradiation in a pristine
lattice, the lines in Refs. 49 and 50 were related to grain
boundaries occurring during the growth. Interestingly, in
Ref. 51, continuing irradiation was found to lead to extremely
thin nanowires of Mo\textsubscript{5}S\textsubscript{4} stoichiometry. Similar wires were
also observed in our experiments.

C. Vacancy dynamics

The rate of identifiable single vacancy diffusion events in
our experiments is fairly small. In order to estimate the rate, we
counted the number of jumps before the start of line formation
and obtained on average 0.023 jumps per second per vacancy
(translating to a diffusion coefficient of 3.8 × 10\textsuperscript{−18} cm\textsuperscript{2}/s).
The events are clearly distinguishable during imaging, where
single image capture takes about 1 s. Examples of diffusion
events are shown in Figs. 3(a)–3(d). In the panel (a), a vacancy
is created presumably in the bottom S layer. This and
another vacancy are seen to diffuse in panels (b)–(d), whereas
other vacancies remain fixed. Indeed, during the experiments,
some vacancies appeared much more mobile, whereas others
remained mostly fixed during the whole imaging period.

We stress that the diffusion is likely caused by the impacts of
energetic electrons, as discussed below. It is expected that for
S in the top layer, the diffusion has very low probability since
the transferred momentum is always downwards. The mobile
and immobile vacancies can then be assigned to vacancies in
the bottom and top layers, respectively.

This is also supported by the calculated migration barrier of
2.3 eV, shown in Fig. 3. This barrier is too high for significant
diffusion at room temperature under thermal equilibrium.
However, the sample is under continuous bombardment by
energetic electrons. In order to check whether diffusion events
could occur under the electron beam, we assign to a sulfur
atom (one of the nearest neighbors to the vacancy) at the
bottom layer kinetic energy corresponding to the amount of
energy transferred to the recoil atom by a high-energy electron
in a binary collision, and carry out molecular dynamics
(MD) simulations to find out whether diffusion event occurs.

A successful reproduction of diffusion events in our MD
simulations required electron energy of 95 keV. This is very
close to the threshold electron energy for vacancy creation
found previously.\textsuperscript{26} Although this value is slightly higher
than 80 kV used in the experiments, a nonzero probability
for these events is expected when the ionic movement at
finite temperatures is accounted for in the cross-section
calculation.\textsuperscript{26}

The SV lines are found to form fairly slowly, and often
via diffusion of single vacancies. In contrast, the formation of
the DV line was usually rapid, often occurring within a time
interval of one frame. Therefore the isolated steps leading to
the line defect could not be resolved. However, as the line was
formed, the nearby vacancies were removed [cf. Figs. 1(b)
and 1(c)], suggesting that the vacancies agglomerated. This
is not consistent with the simple picture of slow vacancy
diffusion rate discussed above. However, our calculations also
suggest that the migration barrier is dramatically lowered, and
thereby the diffusion rate is enhanced, when the number of
vacancies in the nearby S sites (on the same side) is increased.
Figure 5 also shows the calculated barriers when additional S is
removed adjacent to the diffusion path (in the two inequivalent
cases). This can lower the barrier down to 0.8 eV, which makes
the diffusion under 80 kV electron beam significantly faster,
and even makes thermal diffusion possible. We thus propose
that, as the local vacancy concentration increases, the diffusion
barrier may drop considerably and thereby accelerate the drive
to the lowest-energy configuration.

During the formation of a DV line, as it contains vacancies
on both sides of the monolayer, the transfer of S between top
and bottom layers should play an important role. We could not
observe this transfer directly. However, the calculated barrier
for migration between top and bottom layers was found to be
3 eV and displacement threshold around 8.5 eV (110 kV
electron energy). The values are slightly larger than for S
sputtering or for single vacancy diffusion, but this process
cannot be completely ruled out, especially when there are
other vacancies in the nearby sites. During the continuous
generation of new vacancies, the structures of these defect
FIG. 4. (Color online) Lattice strain (shrinkage) as a function of vacancy concentration. The strain is isotropic in the case of isolated vacancies, but strongly anisotropic for vacancy lines. Strains in the direction parallel and perpendicular to the line are denoted by $\epsilon_||$ and $\epsilon_\perp$, respectively. (b) Strain field for DV line defect. The arrows denote atom displacement from its original position in a pristine lattice to its position in a defective lattice. The arrow length is artificially increased for visualization purposes.

lines also evolve in time. Not only do they grow, but also migrate occasionally. An example of DV line migration is seen in Figs. 1(c) and 1(d).

D. The effects of strain on vacancy agglomeration

The strong local lattice contraction around DV lines is evident from Figs. 2(d) and 2(j). Naturally, increasing vacancy concentration leads to contraction of the whole lattice. Figure 4(a) shows the calculated change in the supercell size (in terms of lattice constant) in the directions parallel and perpendicular to the SV and DV line as a function of vacancy concentration. These changes are obtained by minimizing the total energy of the defective system with respect to the supercell size. The case of isolated single vacancies is also shown for comparison. Single vacancies lead to isotropic contraction, while SV lines to slightly anisotropic contraction. In the case of DV lines, the size of the supercell perpendicular to the line $\epsilon_\perp$ contracts strongly, whereas the size parallel to the line $\epsilon_||$ remains close to that of the pristine system. This can also be understood from the strain field of the DV line defect, which is visualized in Fig. 4(b), where arrows denote the atom displacement upon creation of the line. Displacements, and thereby the strain field, extend faraway in the direction perpendicular to the line defect, but affect very little the lattice outside the two end points.

On the other hand, the dependence of the formation energy of line defects on strain shown in Fig. 4 also means that external control of strain in the sample can favor formation of lines of particular orientation. In order to study this, we examined line formation at the freestanding edge of monolayer MoS$_2$. Figure 5(a) shows an HR-TEM image taken in the vicinity of the flake edge. On other sides, MoS$_2$ is clamped to the TEM grid. Initially, the edge is straight. After prolonged electron irradiation, the edge is bent inwards. Due to the instability of the free-standing edge, the resolution at the edge is worse than in the rest of the sample. Most interesting, the majority of the line defects are seen to be directed parallel to the edge. This is enabled by the fact that stress can be released from the direction of the edge, but not from the perpendicular direction.

We propose that the full process leading to preferentially aligned line defects is the following [illustrated in Fig. 6]. (i) With increasing concentration of single vacancies, the lattice may release the stress from the direction of flake edges leaving the sample effectively under tensile strain from lateral directions. (ii) Such nonuniform strain favors formation of lines oriented parallel to edges by more than 50 meV per S vacancy. (iii) Formation of DV lines leads to additional contraction of the lattice perpendicular to the lines, but relieves the stress parallel to the line. Thus, active control of strain during electron irradiation should lead to formation of parallel lines.

For a sample that is clamped at all sides, the formation of line in one direction leads to perpendicular tensile stress, which makes it unfavorable to form further lines parallel to it.

FIG. 6. (Color online) A sketch illustrating the formation and energetics of vacancy lines near the MoS$_2$ flake edge with referential orientation. The energies are normalized to the number of isolated vacancies, and calculated at the 3.1% vacancy concentration.
Consequently, the irradiation should lead to an equal number of lines with different orientations. Both cases have been seen in our experiments, depending on the clamping of the sample.

E. Line properties and substitution energetics

The lines observed in our experiments, and in particular, their directionality, could prove useful in various applications, which we will discuss next. Many material properties are expected to change as directional defects are introduced. For instance, optical response will depend on the polarization of light and catalytic activity may be enhanced for larger vacancy clusters.52,53 Here, we will limit our study on the electrical and magnetic properties of the lines.

It is worth mentioning first, that in addition to electron irradiation, isolated vacancies have been produced by voltage pulsing under the scanning tunneling microscope (STM).54–56 It was also later suggested that vacancy lines could be formed by STM, with calculations showing clearly increased conductance along the lines.57 Such method provides more control than irradiation, although these methods are not easily scalable.

In the case of single vacancy, there is an unoccupied level in the upper half of the gap and an occupied level nearly degenerate with valence band maximum (VBM).33,58 The density of states of the SV and DV lines is shown in Figs. 7(b) and 7(d). In the case of SV line, the DOS is similar to that found in Ref. 57. The unoccupied levels widen to a band covering large portion of the band gap. The occupied vacancy levels do not interact strongly, and the system still retains a gap of about 0.5 eV. In practice, due to the existence of other defects in the system and possible effects of the environment, the Fermi level may lie within the defect band and thereby lead to enhanced conductivity parallel to the lines. In the case of the DV line, the defect band widens further and the band gap closes, thus making the lines truly metallic.

Lines of naked vacancies are likely of very limited practical use due to their reactivity. However, the vacancy lines may be filled, and consequently functionalized, by other atoms as we reported for isolated vacancies.23 When the sample is removed from the TEM chamber, the vacancies should get filled immediately with elements abundant in air such as N, O, and C. Our calculations indicate that, even in the case of fairly strongly reconstructed DV lines, filling of vacancy lines should lead to the same local geometry as if the substitution was carried out one vacancy at a time in pristine MoS2. The density of states for various donor, acceptor, and isoelectronic substitutions to SV and DV lines is shown in Figs. 7(b) and 7(d) with the corresponding substitution energies given in Figs. 7(a) and 7(c). The substitution energy is defined as

\[
E_{\text{sub}} = E_{\text{tot}}(X@Vac) - \left[ E_{\text{tot}}(\text{Vac}) + \mu_X \right],
\]

where \(E_{\text{tot}}(X@Vac)\) and \(E_{\text{tot}}(\text{Vac})\) are the total energies of the supercells with species \(X\) inserted into the vacancy and with the bare vacancy, respectively. For the chemical potential of the substituting species \(\mu_X\), we consider three different references: isolated atoms, dimers, and molecules with hydrogen. The calculations are carried out for infinitely long vacancy lines and the energies are always given per vacancy.

Many of the substitution processes are energetically favorable, depending on the chemical environment. The energies tend to be slightly higher in the case of DV substitution, due to the low total energy of the DV vacancy lines. Therefore, in some cases, the single atom substitution energies given in Ref. 33 may better quantify the stability. O and Se are isoelectronic to S and lead to only minor changes in the electronic structure with respect to pristine MoS2, thus effectively passivating the lines. Although it was previously found that S and Se like to form a random substitutional alloy
under thermal equilibrium, the approach proposed here could be used to circumvent these limitations to engineer lines filled with Se (or Te).

More interesting substituting species are from groups V and VII, as they lead to acceptor and donor doping, respectively. For SV lines, P, As, F, Cl, and Br all lead to formation of defect bands with fairly small band widths, but still predominantly retaining their acceptor and donor characteristics found for filling of isolated vacancies. Common to all these systems is that the substituting atom is more strongly bonded to the Mo atoms perpendicular to the line. This leads to smaller coupling parallel to the line and therefore to narrower defect bands. Nitrogen substitution leads to extremely wide defect band spanning almost the whole gap. This is caused by the strong bonding of N to Mo atoms parallel to the line, which allows coupling between the N atoms and thereby leads to strong dispersion of the impurity band. For DV line substitution, in many cases, the defect bands widen even further. The curious cases here are P and As, which show defect bands in the middle of the gap.

The density of states also often shows spin-polarization. This is the case for all donors studied here, but for acceptors only in the case of As in the SV line. Therefore the conductivity should show spin selectivity in addition to the direction selectivity. Overall, postsynthesis electron-beam-mediated doping can provide more control over the magnetic response of MoS2, as compared to that observed in bulk MoS2, edges of MoS2 flakes, and proton irradiated samples.

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IV. CONCLUSIONS

Our AC-HRTEM experiments indicate that prolonged electron irradiation of monolayer MoS2 gives rise to agglomeration of sulfur vacancies into line defects due to migration of the defects. Different kinds of such extended defects consisting of one or two rows of vacancies were found, and their atomic structures and electronic properties were determined with the help of first-principles calculations. The orientation of line defects is sensitive to mechanical strain, and thus the direction of the lines may be controlled by application of external strain. The line defects can be filled with various impurity species, suggesting a way to alter the electronic and magnetic properties of monolayer MoS2 with line defects. Overall, our results suggest a way for strain and electron-beam-assisted engineering of MoS2-based nanostructures.

Appendix 8

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43. X. Wei, M. Wang, Y. Bando, and D. Golberg, ACS Nano 5, 29162922 (2011).


List of Conference contributions
Appendix 9

The pristine atomic structure of MoS$_2$ monolayer protected from electron radiation damage by graphene

The pristine atomic structure of MoS$_2$ monolayer protected from electron radiation damage by graphene

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Materials can, in principle, be imaged at the level of individual atoms with aberration corrected transmission electron microscopy. However, such resolution can be attained only with very high electron doses. Consequently, radiation damage is often the limiting factor when characterizing sensitive materials. Here, we demonstrate a simple and an effective method to increase the electron radiation tolerance of materials by using graphene as protective coating. This leads to an improvement of three orders of magnitude in the radiation tolerance of monolayer MoS$_2$. Further on, we construct samples in different heterostructure configurations to separate the contributions of different radiation damage mechanisms. © 2013 AIP Publishing LLC.

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Radiation damage is a prevalent challenge when materials are introduced in radiation hostile environments, either on purpose or inadvertently, e.g., in nuclear reactors, space applications, or scientific instruments such as in transmission electron microscopes (TEM). Nowadays, in state of the art TEMs, the sample is imaged using a beam of energetic electrons with energies ranging from 20 keV (Refs. 1, 3) to 300 keV. Hardware aberration correction (AC) in a TEM4, 6 allows in principle direct in situ observation of single atoms1 and single atomic columns3 of materials. However, the instrumental resolution can only be reached when the material can withstand an unlimited electron dose. In practice, this is rarely the case. Therefore, the resolution in the high resolution TEM image is nowadays predominantly limited by the electron dose, which the specimen can tolerate before it is damaged.7

On the other hand, simultaneous production and observation of radiation induced transformations in the sample allow detailed studies of radiation damage in a TEM. Traditionally, second order phenomena, such as fading of diffraction spots connected to the loss of sample crystallinity, mass loss, changes in the energy loss spectra, and electron beam induced x ray yield, have been used for characterization of radiation damage10 in classical three dimensional specimens. Two dimensional (2D) materials, such as graphene, h BN, and MoS$_2$, however, have allowed resolving the electron beam induced changes atom by atom, making a direct observation of radiation damage at the level of the basic building blocks of matter the atoms possible.11-14 A notable difference in bulk materials is that in such 2D materials surface effects are dominating, as in essence, surface is all the materials have.

Radiation damage in the TEM is divided into two different categories, where the first one is related to displacements of atoms through direct collisions between the energetic electrons and target atoms (so called knock on damage), and the second to excitations of the electronic system of the target,15 which can lead, e.g., to radiolysis. Moreover, energy deposition from the electron beam can lead to heating of the specimen and to ejection of secondary electrons. The latter may result in a significant electrostatic charging in insulating materials, which can even lead to a so called Coulomb explosion,16 where heavily charged material disintegrates due to internal electrostatic repulsion. Contaminants on the sample surface and residual gases in the vacuum of the microscope can be broken down, thus creating free radicals, which can lead to a chemical etching of the sample surface.17 Interplay of damage mechanisms is possible, e.g., if the response of the target to knock on collisions is different in an electronically excited or charged state. Theoretical predictions of radiation damage in the TEM have been limited mostly to the simplest case of the knock on process12, 14 since calculations on the other processes are considerably more challenging.

Many approaches have been proposed and employed for combating the adverse effects of electron radiation. On the instrumentation side, lowering the electron energy reduces knock on damage, as there is a material specific threshold in momentum, which needs to be transferred to the target atom in order to displace it from its lattice position. The cost of a lower electron energy, however, is loss in attainable resolution, and thus the aim is to work below, but close to the damage threshold energy. On the other hand, increasing the electron energy lowers the inelastic scattering cross section, thus reducing damage related to the excitations of the electronic system of the target. Depending on which mechanism is predominant in a sample, an optimal electron energy needs to be selected.13, 15

An alternative route for combating radiation damage is treatment of the sample itself. Protecting a specimen by coating it with conducting and/or radiation resistant material is a simple and effective method to increase the electron radiation tolerance of materials by using graphene as protective coating. This leads to an improvement of three orders of magnitude in the radiation tolerance of monolayer MoS$_2$. Further on, we construct samples in different heterostructure configurations to separate the contributions of different radiation damage mechanisms.
when the exit surface of the sample is coated, sputtering of target material can be inhibited. As an extreme demonstration of the benefits of coating a sample, mosquito larvae were recently demonstrated to come out alive and even hatch after investigation in the vacuum of a scanning electron microscope when a coating treatment was applied.\textsuperscript{19}

A typical drawback of coating a specimen, however, is that it obscures the specimen itself, degrades the signal to noise ratio, and consequently reduces the attainable specimen resolution. Therefore, an optimal coating material would have excellent electrical and thermal conductivity, be resistant and highly transparent to electrons at the used energy, be chemically inert, and be crystalline. The last is important as the known image contribution of the crystalline lattice can be removed from the micrographs in digital post processing, e.g., by Fourier filtering.\textsuperscript{20,21} The material meeting all these criteria is graphene, and it has indeed been suggested and employed as the ultimate sample substrate for TEM.\textsuperscript{1,7,18,20,22} The usefulness of graphene in reducing ion radiation damage has been reported in other studies, where significant reduction in the sputtering yield of platinum covered with graphene under ion irradiation has been predicted,\textsuperscript{29} and reduced damage in graphene sandwiched between SiO$_2$ and another graphene layer under ion bombardment has been observed.\textsuperscript{30}

In this study, we show how coating an electron beam sensitive material single layer MoS$_2$ with graphene dramatically improves its electron radiation resistance. We analyse the evolution of the electron radiation damage at atomic resolution, employing 80kV AC HRTEM. We show that the electron radiation resistance of the MoS$_2$ single layer is increased by nearly three orders of magnitude when it is sandwiched between two graphene layers, as compared to the free standing MoS$_2$ layer (see Fig. 1). This demonstrates the effectiveness of our graphene sandwich approach in fighting radiation damage. In addition, by preparing samples in different heterostructure configurations, we are able to separate the role of the different damage mechanisms in the material at the level of single atoms.

For this purpose, we constructed samples in four different configurations, using the following procedure: A graphene flake (1-3 layers) was mechanically exfoliated from graphite, deposited on SiO$_2$(90 nm)/Si, and transferred to Quantifoil grids using KOH.\textsuperscript{31} Single layer MoS$_2$ was also cleaved from a natural crystal, and deposited on SiO$_2$/Si. In order to transfer the MoS$_2$ flake to the already transferred graphene, we positioned the graphene/Quantifoil on the top of the single layer MoS$_2$. Once positioned, the MoS$_2$ layer was transferred via the same method as used for graphene. This process was repeated for another graphene layer. As a result, we got a sandwich structure, where the MoS$_2$ layer lays in between graphene layers. The HRTEM investigations were performed in an aberration corrected FEI TITAN 80 300 operated at 80kV with C$_{\text{c}}$ 0.03 nm under Scherzer conditions. The vacuum level in the microscope was <10$^{-7}$ millibars.

As the baseline sample, we used a free standing MoS$_2$, which was also the subject of an earlier study.\textsuperscript{14} For evaluating the ultimate protective power of the graphene layers, the sandwich structure was constructed (named the G/MoS$_2$/G configuration), where the MoS$_2$ layer was enclosed between graphene layers via subsequent transfer of the mechanically exfoliated layers on to a TEM grid at the same position (see Fig. 1(a) for a schematic representation). For separating the effects of the different damage mechanisms, two heterostructures with MoS$_2$ monolayer and graphene were constructed, with graphene either on top or bottom of the MoS$_2$ layer (named the G/MoS$_2$ and MoS$_2$/G configurations).

Based on light micrographs produced during sample preparation, the correct sample area was located at low magnification in the TEM in order to minimize the electron dose before the characterization of the effects of the electron beam on the material. Electron diffraction patterns were recorded for verifying the monolayer nature of the MoS$_2$,\textsuperscript{25} at the area under investigation. A diffractogram of the G/MoS$_2$/G sample is presented in Fig. 1(b), showing the two graphene peaks originating from the top and bottom layers, and the peaks of alternating intensity from the MoS$_2$ monolayer.

![FIG. 1. The effect of sandwiching MoS$_2$ single layer in between graphene layers (the G/MoS$_2$/G configuration). (a) A schematic representation of the sandwich structure, where a MoS$_2$ monolayer is confined in between two graphene layers (green spheres are Mo, yellow spheres are S, and white spheres are C). (b) Electron diffraction pattern of the G/MoS$_2$/G sample, showing the monolayer MoS$_2$ peaks at 3.7 nm$^{-1}$ and the two graphene peaks at 4.7 nm$^{-1}$ in different orientations, originating from the top and bottom layers. The ratio of the alternating intensities of the first-order reflections of the MoS$_2$ maxima is 1:20, confirming its monolayer nature (see Ref. 31). (c) An 80kV AC-HRTEM image of free-standing MoS$_2$ monolayer after an electron dose of 2.8 × 10$^8$ e/nm$^2$. Serious damaging of the sample can be observed. (d) An 80kV AC-HRTEM image of the G/MoS$_2$/G sample after an electron dose of 2.8 × 10$^9$ e/nm$^2$. (e) The frame of panel (d) after Fourier filtering the graphene contribution out. Here the electron radiation damage is dramatically reduced, and, e.g., determination of the MoS$_2$ edge structure is possible. The scale bars are 2 nm.](image-url)
Once the correct sample area was located, the material was observed in the high resolution mode, while keeping track of the total accumulated electron dose. All the samples were investigated in similar conditions in terms of vacuum level, dose rate, magnification, and total beam current. Importantly, atomically clean areas were found in the heterostructure areas, which corroborate the earlier observation by Haigh et al.\textsuperscript{33} There interfaces in similar heterostructures were found to be contamination free, and in full contact in cross sectional images. Similar to what was observed in our earlier study,\textsuperscript{34} exclusively sulphur vacancies are created under the electron beam. By observing the rate at which the vacancy concentration increases, one can directly evaluate the total vacancy production cross section in each case.

The dramatic effect of the graphene layers in the G/MoS\textsubscript{2}/G sample can be seen when panels 1(c) and 1(d) are compared. In panel (c), the free standing MoS\textsubscript{2} sample is seriously damaged after an electron dose of 2.8 $\times$ 10\textsuperscript{8} e/\textmu m\textsuperscript{2}, and the vacancies have partly rearranged into lines, as described in Ref. 34. Consequently, no information on the atomic structure of the pristine state of the sample can be extracted. With G/MoS\textsubscript{2}/G sample (panel (d)), the situation is completely different after the same electron dose. Here, for example, the structure of the MoS\textsubscript{2} flake edge can be readily observed at atomic resolution, which would not be possible with the unprotected sample, and the vacancy concentration in the flake remains very low. Panel (e) shows the same HRTEM frame as in panel (d), but after filtering out the graphene contribution and high frequency noise by means of Fourier filtering, which further improves the interpretability of the MoS\textsubscript{2} structure by removing the Moiré effect resulting from the overlay of the MoS\textsubscript{2} and the graphene lattices.

For quantifying the damage rate and for studying the contributions of the different damage mechanisms, all the four samples were given an electron dose at which the vacancy concentration increased up to 4%, and HRTEM images before and after the irradiation were compared, taking into account the increase in vacancy concentration. The relevant measured quantities are given in Table 1, along with the calculated vacancy production cross sections. The cross sections are calculated by $\sigma = \Delta N/N_0$, where $\Delta N$ is the number of lost S atoms, $N$ is the total number of S sites in the investigated area, and $\phi$ is the accumulated electron dose.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta N$</th>
<th>$N$</th>
<th>$\phi$ (e/\textmu m$^2$)</th>
<th>$\sigma$ (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS\textsubscript{2}</td>
<td>116</td>
<td>3176</td>
<td>8.2 $\times$ 10\textsuperscript{7}</td>
<td>4.5(4)</td>
</tr>
<tr>
<td>G/MoS\textsubscript{2}</td>
<td>43</td>
<td>2984</td>
<td>9.7 $\times$ 10\textsuperscript{7}</td>
<td>1.5(2)</td>
</tr>
<tr>
<td>MoS\textsubscript{2}/G</td>
<td>177</td>
<td>5294</td>
<td>7.0 $\times$ 10\textsuperscript{8}</td>
<td>0.48(4)</td>
</tr>
<tr>
<td>G/MoS\textsubscript{2}/G</td>
<td>5</td>
<td>3090</td>
<td>2.14 $\times$ 10\textsuperscript{9}</td>
<td>0.008(3)</td>
</tr>
</tbody>
</table>

The pristine atomic structure of MoS\textsubscript{2}
after the electron dose, which completely destroyed the free standing target. We would like to point out that we do see occasional migration steps of MoS2 layers also in the G/MoS2/G configuration (the locations of the vacancies in the G/MoS2/G frames in Fig. 2 are not identical). See supplemen
tary material15 for a further demonstration of the differ ence between damage rates in the G/MoS2/G and the G/MoS2/G configurations, where a spot in the G/MoS2/G sam
ples was located, at which the bottom graphene layer ends, thus allowing the observation and comparison of fully and half covered parts at the exact same conditions.

The cross sections for the MoS2, G/MoS2, MoS2/G, and G/MoS2/G configurations were determined to be 4.5(4) b, 1.5(2) b, 0.48(4) b, and 0.08(3) b, respectively, (1 b equals \(10^{-24}\) nm²), the number in parenthesis denotes the one sigma confidence interval of the last digit(digits). As compared to the free standing case, the cross section is reduced by a factor of 2.9 for the G/MoS2 configuration, 9.3 for the MoS2/G confi


guration and 600 for the G/MoS2/G configuration. If one defines the critical electron dose to be the dose at which 5% of target sulphur atoms are lost, one gets values of 1.12(11) \times 10^{10} e/nm², 3.3(5) \times 10^{11} e/nm², 1.05(8) \times 10^{13} e/nm², and 6(3) \times 10^{16} e/nm² for the MoS2, G/MoS2, MoS2/G, and G/MoS2/G configurations, respectively. Quantification of dam age in the graphene layers is not possible due to the much stronger contrast originating from the MoS2 layer. However, prior studies have shown that graphene is quite robust under 80 keV electron beam and tends to flexibly reorganize into a closed network in the presence of vacancy type defects.12,16

By comparing the samples in the G/MoS2 and MoS2/G configurations, it can be seen that knock on damage is not the dominant damage mechanism in MoS2 under the electron beam, contrary to what was assumed in our earlier paper.14 Due to standard collision kinetics, the sample atoms are always displaced away from the beam exit surface of the sample, and the graphene layer on the exit sur face inhibits their ejection. If suppression of knock on dam age is taken to be only the difference between the two configurations, one can estimate the contribution of the knock on process by simple subtraction of the two cross sections. A value of 1.1(2) b is acquired, which is only 24% of the total damage cross section in the free standing case and consequently, 76% of the damage is of a different origin. This knock on cross section is in good agreement with the theoretical prediction of 0.8 b.14 It should be pointed out that the theoretical value is based on a displacement threshold calculated specifically for sulphurs in the bottom layer, which is easier to displace than the top layer sulphurs.

Comparison of the samples with only single side covered and the free standing MoS2 sample allows studying the effects of the other damage mechanisms, although clearly iso
trating the mechanisms is not as straightforward as in the case of knock on damage. If one assumes that already covering a single side of the MoS2 layer with graphene suppresses the damage processes caused by electronic excitations and charg
ing, and thus only chemical etching on one surface is active in the MoS2/G configuration, one can further calculate a cross section of 2.4(6) b as the contribution related to elec
tronic excitations and charging (55% of the free standing cross section). This number, however, should be taken as a rough estimate. In future experiments, it would be of great in terest to replace the graphene layer on one or both surfaces by a hexagonal boron nitride layer, which is chemically inert, has comparable mechanical properties to those of graphene, but is an insulating material. Such samples would allow fur ther separation of the different damage mechanisms.

To conclude, we have applied graphene as a coating ma terial for dramatically reducing radiation damage in single layer MoS2 induced by the 80 keV electrons used for high resolution imaging in AC HRTEM. Our sample prepa ration method allows characterization of the pristine atomic structure of a radiation sensitive material. Moreover, we dem

onstrated the usefulness of different layered graphene MoS2 heterostructures in separating different radiation damage mechanisms. The technological implications are obvious: Using graphene as a protective layer is highly advantageous when imaging radiation sensitive materials in a transmission electron microscope, from thin layers to isolated molecules. This expands the applicability of the AC HRTEM signifi cantly, as radiation damage has been a serious hindrance in fully exploiting the greatly improved resolving power of the aberration corrected instrument. The total vacancy crea
tion cross section was reduced 600 fold going from a free standing MoS2 layer (4.5(4) b) to the sandwiched config
uration (0.08(3) b). The contribution of knock on damage was separated from the total damage cross section (1.1(2) b), and was observed to only partially explain the total accumu lated damage. An estimate on the cross section related to electronic excitations was deduced (2.4(6) b), although heter ostructures of different materials would be useful in address ing this effect more reliably. Other types of displacing damage were not explicitly studied here, but our results sug

gest that graphene can be used also more generally in protect ing surfaces from radiation damage.

Note Added in Proof: During the reviewing of this work, it has come to our attention that R. Zan et al. have recently and independently reported similar results to ours, but using focused beam scanning TEM17 instead of broad illumination TEM.

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Author Contributions: G.A.S., S.K., and U.K. conceived

and planned the experiments. M.S. prepared the samples under the supervision of G.A.S., and S.K. S.K. executed the HRTEM imaging under the supervision of U.K. All the authors contributed to the analysis of the data. O.L. wrote the manuscript with assistance from U.K. and all the authors.

The pristine atomic structure of MoS$_2$
Appendix 10

Direct Imaging of a Two-Dimensional Silica Glass on Graphene


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Direct Imaging of a Two-Dimensional Silica Glass on Graphene

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ABSTRACT: Large-area graphene substrates provide a promising lab bench for synthesizing, manipulating, and characterizing low-dimensional materials, opening the door to high-resolution analyses of novel structures, such as two-dimensional (2D) glasses, that cannot be exfoliated and may not occur naturally. Here, we report the accidental discovery of a 2D silica glass supported on graphene. The 2D nature of this material enables the first atomic resolution transmission electron microscopy of a glass, producing images that strikingly resemble Zachariasen’s original 1932 cartoon models of 2D continuous random network glasses. Atomic-resolution electron spectroscopy identifies the glass as SiO2 formed from a bilayer of (SiO4)2− tetrahedra and without detectable covalent bonding to the graphene. From these images, we directly obtain ring statistics and pair distribution functions that span short-, medium-, and long-range order. Ab initio calculations indicate that van der Waals interactions with graphene energetically stabilizes the 2D structure with respect to bulk SiO2. These results demonstrate a new class of 2D glasses that can be applied in layered graphene devices and studied at the atomic scale.

KEYWORDS: two-dimensional glass, 2D silica, SiO2, transmission electron microscopy, graphene imaging substrates, Zachariasen’s model

In stark contrast with two-dimensional (2D) crystals such as graphene and monolayer hexagonal boron nitride, 2D glasses remain almost completely unexplored. Reducing the dimensionality of amorphous materials would enable their direct, atomic resolution structural and chemical characterization, a long-standing challenge in amorphous materials.5,6 These materials, particularly if they can be isolated from substrates and freely manipulated, may have enormous applicability.

Figure 1a,b shows Zachariasen’s original 1932 model of a continuous random network.6 In this model, amorphous structures differ from crystalline ones simply by allowing variable bond angles, which introduce structural disorder while maintaining chemical order. In 2D, this creates amorphous structures that contain continuous networks of rings of different sizes (Figure 1b). Determining the structure of amorphous materials and comparing them to theoretical models such as Zachariasen’s has remained challenging. In principle, transmission electron microscopy (TEM) and scanning TEM (STEM) possess sufficiently high resolution to resolve atomic spacings in disordered systems, particularly after recent developments in aberration-correction.7,8 These techniques, however, typically produce images which are 2D projections of 3D structures. In these 2D projections, disorder in materials renders direct atomic-scale imaging almost impossible.9,10 We sidestep the projection problem by imaging a 2D glass. Crystalline two-dimensional oxides, formed from mono- or bilayers of silica tetrahedra, have recently been grown on metal substrates.11–13 These materials are natural starting points for amorphous 2D glasses because silica is a ready glass former and contains directional bonds, a necessity for forming a disordered continuous 2D network. Here, we show that preparation of the amorphous phase of 2D silica, coupled with a graphene support,14–16 allows atom-by-atom (S)TEM imaging and spectroscopy of a glass. During the final preparation of this manuscript, another group, using scanning tunneling microscopy, has observed an amorphous phase of 2D silica grown on bulk Ru(0001).17 Our results demonstrate that the silica can also be grown with graphene on copper foils and isolated from the metal surface; we also detail rigorous analyses of the...
structure, bonding, and thickness of the material, and the nature of the graphene silica interface.

Figure 1c-f shows atomic-resolution annular dark-field scanning TEM (ADF-STEM) images (c,d) and corresponding diffractograms (e,f) of crystalline and amorphous regions of a 2D silica glass supported by graphene. The weakly scattering graphene substrate is not apparent in these images without filtering. As we demonstrate later, the bright spots in ADF images represent stacks of silicon and oxygen atoms, while individual oxygen atoms appear as an increase in intensity between the bright spots (see Supporting Information). The strong qualitative match between these images and Zachariasen’s model suggests that these images are of a 2D glass that roughly obeys the continuous random network model. Scale bars 5 Å. (c,f) Fast Fourier transforms (FFTs) of STEM images from amorphous and crystalline regions. Spots inside the gold-colored region are from silica; spots immediately outside this region are graphene spots. Other spots can be either graphene or silica. In the silica-only (gold) regions, the amorphous silica exhibits no clear reflections, a contrast with the crystalline FFT. The silica crystalline lattice constant is 5.3 Å, roughly 2.14 times that of graphene. (e,f) Fast Fourier transforms (FFTs) of STEM images from amorphous and crystalline regions. Spots inside the gold-colored region are from silica; spots immediately outside this region are graphene spots. Other spots can be either graphene or silica. In the silica-only (gold) regions, the amorphous silica exhibits no clear reflections, a contrast with the crystalline FFT. The silica crystalline lattice constant is 5.3 Å, roughly 2.14 times that of graphene. (see Supporting Information). This large 7% lattice mismatch along with the presence of amorphous regions suggests that the silica is not covalently bonded to the graphene on large scales. We see no evidence for local regions that are coherently strained to be lattice-matched with the graphene. Figure 2 shows large-area TEM and STEM images of the silica. Different regions of the material range from predominantly polycrystalline (Figure 2a) to predominantly amorphous (Figure 2c) in which large areas appear to be continuous random networks. Most of the material resembles the region shown in Figure 2b, which contains mostly amorphous material with some crystalline inclusions. We attribute the mixing of crystalline and amorphous phases to growth kinetics. Additional non-silicon atoms are sometimes present in or near the center of rings, introducing small amounts of chemical disorder.

We used STEM electron energy-loss spectroscopy (EELS), which measures the local unoccupied partial density of states,18,19 to map the composition and bonding of the glass. Figure 3a-c contains atomic-resolution maps showing the distributions of silicon, carbon, and oxygen in the region shown in Figure 3d. Figure 3e-g shows the corresponding EEL...
Figure 2. Large-area TEM and STEM images showing different phases of 2D silica ranging from predominantly crystalline to amorphous. (a) A smoothed TEM image of a predominantly crystalline region. Crystals are joined by grain boundaries similar to those in polycrystalline graphene. (b) A TEM image of a typical region of glass, which contains both amorphous regions and crystalline inclusions such as that seen in the bottom right, which range in size from just a few unit cells up to tens of nanometers across. (c) A smoothed ADF-STEM image of an extended amorphous region formed primarily from a continuous random network of rings. Scale bars 2 nm.

Figure 3. Atomic resolution EELS identifies the 2D glass as SiO$_2$, a bi-tetrahedral layer of silica. (a c) EELS concentrations maps of Si, C, and O of a region of bilayer graphene partly covered by 2D glass (top half). The O map has been smoothed to improve contrast. (d) Corresponding ADF image. In the bottom portion of the image, the glass is damaged and largely removed with a few Si atoms clinging to the edge of the graphene sheets (bottom left). Unlike the SiO$_2$-like bonding in undamaged glass, these Si atoms have SiC-like fine structure, suggesting they have bonded to the graphene edge. Scale bar 2 nm. (e g) Raw (black diamonds) and smoothed (black lines) experimental EEL spectra of the 2D glass plotted with reference data (green lines) for bulk a-SiO$_2$ and FEFF simulations (blue, red). (h) Side view cartoon of the structure suggested by EELS measurements.
spectra from the glass. The glass seen in the top portion of the ADF image corresponds with EELS maps of silicon and oxygen, suggesting that the glass is silicon oxide. We analyzed the images and spectra in Figure 3 to construct a 3D model of the atomic structure and thickness of the silica. First, the Si-L2,3 edges in the glass are similar to bulk SiO2 reference EELS edges, a strong indication that the Si atoms are tetrahedrally bonded (SiO4)2− units. In contrast, silicon atoms from damaged areas (Figure 3a, bottom) have a Si-C-like fine structure that indicates that they have bonded to the graphene edge (Supporting Information). Additionally, the intensity and fine-structure of the C K edge (Figure 3f) are consistent with bilayer graphene20 and do not show any indications of covalent C–O bonding. Finally, we observe a peak at 536 eV in the O K edge (Figure 3g). To understand the origin of this peak, we performed ab initio simulations using FEFF9 21 of two crystalline silica structural models of different thicknesses, which we term mono- and bi-tetrahedral (Supporting Information). These simulated O K edges are plotted along with the experimental spectrum in Figure 3g. While the mono-tetrahedral structure lacks the peak observed in experiment, a good agreement is found for the bi-tetrahedral structure, shown in Figure 3h. This difference occurs because the O K edge peaks damp out when O atoms have fewer than 6 O nearest-neighbors,22 23 a condition met by a bilayer but not a monolayer of silica tetrahedra. Additional quantitative measurements of the amplitudes of ADF and EELS signals on the film also are within experimental error of the bilayer structure and exclude the mono-tetrahedral structure and structures which are ≥3 tetrahedra thick. (Supporting Information).

Figure 4 shows top and perspective cartoons of the bi-tetrahedral silica structure on graphene suggested by our data. The structural building blocks are similar to those recently reported in 2D silica on bulk Ru(0001), also composed of a bilayer of silica tetrahedra.13,17 This structure places every atom in a local environment similar to bulk SiO2 in which all bonds are satisfied. Unlike its crystalline analogue, the amorphous 2D silica has a unique structure where tetrahedra are disordered in two dimensions but ordered in the third dimension, where the upper and lower tetrahedra are locked in registry. This structure is therefore a 2D glass in the sense that it is single unit cell thick, analogous to 2D atomic crystals such as MoS2 or NbSe2.

We extend the atomic scale analyses above by examining the pair distribution function (PDF) and ring statistics. PDFs, which statistically describe atomic spacings, have played an important role in distinguishing between paracrystalline and continuous random network glassy models. Ring statistics are also instrumental because they can differentiate structural models whose PDFs are indistinguishable.24,25 Ring statistics, however, are difficult, if not impossible, to measure directly in 3D glasses. These two standard metrics of structural models in glasses provide a quantitative measure of short, medium, and long-range order in our 2D glass and allow comparison to theoretical models for 2D and 3D glasses.

Figure 5a,b shows 2D-projected partial Si–Si pair-distribution functions (PDFs) in crystalline and amorphous regions extracted from Si positions in real-space images. On short ranges, on the order of 0.5 Å, the first peak in each pair-distribution functions represents Si Si nearest neighbor spacings. For medium ranges on the order of 5–20 Å, the pair distribution functions of the crystalline and amorphous regions begin to diverge; peaks in the amorphous Si Si pair distributions become strongly damped. The second peak in the amorphous PDF around 4.3 Å is almost as sharp as the first one, a notable difference from 3D silica.26 This likely corresponds to the reduced set of possible Si Si bond angles that occur in 2D in order to provide ring closure. At long ranges >20 Å, the crystalline PDF maintains sharp peaks while the amorphous PDF is featureless.

Figure 5c plots a histogram of ring size in crystalline and amorphous regions extracted from large area images (Supporting Information). In this plot, the ring size refers to the number of vertices visible, or the projected number of tetrahedral units. In the amorphous material, we observed stable rings ranging from 3 to 10 tetrahedra in size (see Supporting Information) with an expectation value of 6.04 ± 0.024 (s.e.m.) tetrahedral units in-plane. Figure 5d compares our experimental ring statistics to a few selected theoretical models: a purely geometrical model for a 2D glass and two molecular dynamics simulations for 3D silica using different interaction potentials.27,28 None of the models fit our experimental results.
kinetics, and cooling rates. As direct experimental measurements of ring size distributions, these results show the distance that separates experiment and theory and should aid in improving models of connectivity in glasses.

We constructed ab initio models of a periodic bi-tetrahedral 2D silica to assess its stability, structure, and electronic properties (Supporting Information). The relaxed bi-tetrahedral structures (Figure 4) closely match our experimental results, and their calculated band structure is similar to bulk SiO$_2$ (Supporting Information). Our energetic calculations indicate that in vacuum, the binding energy of the bi-tetrahedral structure is 86 meV per structural unit higher than bulk silica. Adding vdW interactions to monolayer graphene energetically stabilizes the bi-tetrahedral silica over bulk SiO$_2$ by 107 meV per structural unit. Covalent bonding to unstrained graphene is a higher-energy state than the van der Waals bonded structures, likely because covalent bonding would result in a large 7% strain and disruption of the conjugated π-system in graphene. Our calculations therefore indicate that graphene, in addition to providing a support membrane, can stabilize new 2D materials.

Coupling ultrathin glasses with graphene support membranes frees these materials from the requirements of extreme mechanical stability, low reactivity, and isolation via exfoliation that have so far limited the range of 2D materials that could be easily identified, processed, and applied. Further, this new class of materials likely includes additional 2D glasses such as alumina or boric oxides and may be applicable in layered graphene devices. Because the silica glass can be easily removed from the copper substrate and contains no dangling bonds, it may also find application in semiconductor or layered graphene electronics as a passivated starting layer for gate insulators.

- ASSOCIATED CONTENT
- Supporting Information
  Growth and sample preparation, image acquisition parameters, additional film structure information, details of elemental, bonding, and structure analysis, image simulations, and DFT structure and energetic simulations. This material is available free of charge via the Internet at http://pubs.acs.org.

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  P.Y.H. acquired and processed STEM and EELS data and conducted structure analysis, R.M.H. performed multislit images simulations, and Q.M. conducted FEFF9 simulations, all supervised by D.A.M. S.K. discovered the material, acquired and processed HRTEM and diffraction data. and participated in DFT calculations. J.C.M. contributed to HRTEM and diffraction experiments. A.S and V.S. grew the material and prepared TEM samples under supervision by J.S. J.K. and A.V.K. constructed the structural models and conceived and carried out the DFT simulations assessing the relative stability and electronic properties of the different models. U.K. supervised the HRTEM work and assembled the team. P.Y.H. and D.A.M. wrote the paper with assistance from S.K. and U.K. All contributed to the discussion of results and their implications and commented on the paper.

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Appendix 10

Nano Letters

Supplementary Information - Direct Imaging of a 2D Silica Glass on Graphene

Supporting Information for
“Direct Imaging of a Two-Dimensional Silica Glass on Graphene”

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1. Growth

The silica/graphene films were discovered by accident. While we were unable to reproduce these results in other furnaces, we detail here the known conditions under which the films were grown. These conditions were sufficient to form several samples of the 2D layer of silica across months using the setup at Max Planck.

The graphene/silica films were prepared with a low pressure CVD technique using hexane as a precursor on polycrystalline Cu foils. The Cu foil was attached to a quartz substrate and placed into a quartz tube. The tube was pumped down to a pressure of \(10^{-2}\) mbar. Then, forming gas (Ar/(5%)H\(_2\)) was introduced at a pressure of \(\sim 5\) mbar and the Cu foil was heated up to 950°C. When the desired temperature was achieved, the forming gas flow was interrupted and hexane vapor was introduced into the quartz tube instead under a pressure of 0.5 mbar for 1 minute. Finally, the sample was cooled to room temperature under the flow of forming gas at a pressure of \(\sim 5\) mbar. These conditions are similar to those described in Reference \(^1\). We speculate that the formation of a 2D layer of silica is due to an unintentional leakage of air into the quartz tube when switching from forming gas to hexane, causing the oxidation of the copper surface and a reaction with the quartz substrate at the contact surface with the oxidized copper. Bi-tetrahedral silica has been recently reported on ruthenium\(^2,3\), and similar conditions may also work for silica growth on copper.

2. Sample Preparation

Graphene/silica films were transferred from the copper substrate by etching in 15% nitric acid and fishing the floating film (without polymer support) onto commercial TEM grids (Quantifoil R1.2/1.3 holey carbon film on Au 200 mesh). Afterwards, the specimen was rinsed in distilled water and dried in dry nitrogen. Prior to TEM, the samples were heated in air to 200°C for 10 minutes; prior to STEM, samples were annealed at 130°C for >8 hours in ultra-high vacuum.
3. TEM and STEM acquisition

TEM experiments were performed with an image-side corrected FEI Titan 80-300 microscope operated at 80kV. The spherical aberration was set to approximately 20µm, and the energy spread of the source was reduced by lowering the extraction voltage to 2kV.

ADF-STEM images were acquired in the NION100 UltraSTEM using a 60keV electron beam with a convergence angle of 25-33 mrad and collection with high- or medium-angle annular dark-field (HAADF and MAADF) detectors. The HAADF detector has a collection angle near 90 mrad. Acquisition times were typically around 40µs/pixel. The parameters produced a probe size near 1.3 Å with imaging conditions similar to those in References 4-6. When processed, ADF-STEM images were low-pass smoothed using the “Smooth” command in Gatan’s Digital Micrograph program and labeled as “smoothed” in figure captions.

4. Film structure, lattice parameters, and uniformity

Supp. Figure 1 shows further examples of high-resolution TEM images. Dark-field imaging was a versatile tool to overcome the lack of contrast in bright field at low magnifications (see Supp. Figure 1a). Supp. Figure 1b demonstrates that the silica is also stable on single-layer graphene, as can be seen from the zoomed in image and its FFT (Supp. Figure 1c and d).
Supplemental Figure 1 | Additional TEM images and FFTs. a) Low magnification image of the silica film on graphene. The inset is a dark-field image of the same region where the covered areas are clearly detectable and partially colored. b) Silica on single-layer graphene as can be seen from d) the FFT of the zoomed-in image c) where only one graphene orientation is present.

Nanobeam diffraction was performed for crystalline and amorphous regions of the silica (Supp. Figure 2 c,d) to complement STEM FFTs (Supp. Figure 2 a,b). Because the crystalline areas are very small, it was necessary to work with a converged probe for nanodiffraction, using a small 50 µm condenser aperture. The 7% lattice mismatch between graphene and silica is clearly detected.

Supplemental Figure 2 | STEM FFTs and TEM nanodiffraction showing amorphous and crystalline 2D silica, as well as the lattice mismatch between graphene and crystalline 2D silica. In c and d, reflections from the silica are contained within the yellow circles. The strongest diffraction spots, outside the yellow circles, are due to the polycrystalline graphene support.
5. EELS acquisition and elemental identification

EELS data were acquired as spectrum images using the NION100 UltraSTEM. The core-loss spectrum image represented in Figure 3 contains 64x64 pixels at 40 milliseconds/pixel and 0.5 eV/channel dispersion to include the Si-L$_{2,3}$, C-K, and O-K edges. Each edge was then background-subtracted using a power-law background model in ImageJ using the Cornell Spectrum Imager (CSI) software developed by Paul Cueva et al. To improve signal-to-noise, we held the power-law subtraction constant over several pixels using the “Oversampled” command with a radius of 6 pixels. This effective background smoothing gave qualitatively similar results as pixel-by-pixel background subtraction. After this processing, we integrated over an energy range within the background-subtraction fitting region to confirm no artificial signal was present.

To generate the spectra in Figure 3 e-g, the background-subtracted spectra from roughly the top-half of the spectrum image, which correspond to un-damaged glassy regions, were averaged. Raw data are plotted as black diamonds. The diamonds are connected with black lines representing the data smoothed using a Savitsky-Golay filter in the energy direction. The oxygen edge, which was weaker and noisier than the others, was more heavily smoothed. The edges were then plotted against reference spectra of SiO$_2$. The reference spectrum in Figure 3e was acquired on a cross-sectioned, thermally oxidized Si wafer using similar acquisition and processing parameters.

To produce the spectrum maps in Figure 3a-c, we integrated over the background-subtracted Si-L$_{2,3}$, C-K, and O-K edges. To increase signal-to-noise, the O map in Figure 3c was low-pass smoothed using the “Smooth” function in Gatan’s Digital Micrograph Program. We performed multivariate curve resolution (MCR) and nonlinear least-squares fitting to characterize the bonding states of the Si atoms. While Si atoms in the glass produce Si$^{4+}$ edges similar to those of SiO$_2$ reference EELS edges, Si atoms attached to graphene edges form SiC-like bonding (Supp. Figure 3).
**Supplemental Figure 3 | Si L$_{2,3}$ EELS edge fine structure.** a) MCR map separating Si concentration into SiO$_2$-like (green) and SiC-like (white) components. b) Si L$_{2,3}$ extracted from MCR analysis. The edges in each pixel in a were fitted to these edges using nonlinear least-squares fitting to make a map of SiC and SiO$_2$ bonding states. c) Reference Si edges corresponding to SiO$_2$, SiC, and Si. The edge in b most closely match the SiO$_2$ and SiC edges, suggesting the glass is SiO$_2$-like, while the damaged Si atoms have SiC-like bonding to the edge of the graphene.

### 6. Determinations of film thickness: ADF imaging

Because local contrast in ADF-STEM imaging scales roughly with the atomic number $Z^n$, quantitative analysis of image intensities can provide mass-thickness information. We measured the mass-thickness of the material using graphene as a reference. Supp. Figure 4a plots the averaged intensities of ADF images of the silicate on various thickness of graphene along with the intensities expected for the theoretical candidate structures (See also Supp. Figure 8). From these data, we extract a mean, silica-only ADF intensity of $3.5 \pm 0.5$ (s.d.) times the intensity of graphene. This value is consistent with a bi-tetrahedral silicate structure.

For comparison to ADF data, we plotted two models in Supp. Figure 4a. In the first, we use an incoherent imaging approximation to generate average intensities. These values take into account only the average density of each element and apply a $Z^n$ model with $1.5 < n < 2$ to account for uncertainty in collection and convergence angles. Using a $Z^{1.7}$ incoherent approximation, for example, the ADF intensity should be 1.8 times the intensity of graphene for a monolayer or 3.3 for a bilayer of (SiO$_4$)$^{2-}$ tetrahedra.
Supplemental Figure 4 | Thickness measurements using quantitative high-angle ADF intensities and a graphene standard. a) Plot of ADF intensity versus graphene thickness for experiment (filled symbols), compared with multislice (empty symbols) and incoherent models (shaded bars). The data most closely correspond with the bi-tetrahedral structure in both simulations. b) Multislice simulation of an image of bi-tetrahedral silica on single-layer graphene. c) Experimental image of crystalline silica on graphene.

For a more rigorous comparison to ADF data, we simulated dark-field detector signals using numerical scattering calculations in E.J. Kirkland’s multislice code. In this code, a full quantum mechanical multiple scattering simulation of electrons is propagated through multi-layered atomic membranes, producing quantitative simulations of dark field detector signals. Atomic scattering factors are characterized by a 12-parameter fit of Gaussians and Lorentzians to relativistic Hartree-Fock calculations. With the inclusion of frozen phonons—where lattice vibrations are modeled by stochastic atomic displacements—multislice has been demonstrated to quantitatively match experimental detector intensities when the specimen, probe, and detector geometries are known.

We set up the code, inputting the experimental conditions discussed in Section 3 and theoretical mono- and bi-layer silica structures on varying thicknesses of graphene. We then extracted
simulated images such as Supp. Figure 4b and averaged intensities versus graphene thickness, plotted in Supp. Figure 4a along with experimental data. To match theory to experiment, we found it was important to include phonon-induced displacements of ~1 Å for carbon atoms and ~0.8 Å for Si atoms. With these values, multislice simulations for bi-tetrahedral silica match both qualitatively (Supp. Figure 4 b,c) and quantitatively (Supp. Figure 4a) with experimental data.

7. Determinations of film thickness: Quantitative EELS

We acquired a second measure of the silicate thickness by doing quantitative EELS (Supp. Figure 5). We first acquired “full” EEL spectra containing Si, C, and O edges as well as the elastic, or zero-loss, signal by recording core-loss spectrum images followed by short-acquisition low-loss spectrum images in the same region. The two energy ranges in each spectrum image were stitched together in each pixel by aligning and scaling spectra so the intensities and peak positions matched in an overlap region.

By acquiring full EEL spectra, we can compare the integrated intensities of background-subtracted core-loss edges as a fraction of the elastic signal to known Si, C, and O inelastic scattering cross-sections\(^{11}\). We used reference scattering cross-sections from Gatan’s EELS atlas\(^{12}\), adjusted for a convergence angle of 25 mrad and a collection angle of 60 mrad. From a continuous 2D silica sheet, we extracted areal densities of 17 ± 3 (s.d) atoms/nm\(^2\) for Si and of 39 ± 7 (s.d.) atoms/nm\(^2\) for O. To within error, these values are consistent with expected values for the bi-tetrahedral structure: 17 atoms/nm\(^2\) for Si and 33 atoms/nm\(^2\) for O.
Supplemental Figure 5 | Thickness measurements using quantitative EELS on an absolute scale.  

**a)** A semi-log plot of a representative EEL spectrum, including the zero-loss peak and Si, C, and O core-loss edges (highlighted in red). We measured the area under these edges as a fraction of the elastic signal in the zero-loss peak to extract areal densities of each element. **b)** A table summarizing EELS measurement of elemental densities and comparing them to expectations for mono-tetrahedral and bi-tetrahedral models.

To confirm that these values were correct, we repeated these calculations for a thermally-oxidized silicon wafer, which provided an Si/SiO$_2$ interface. We measured the thickness of the samples using the ratio of the inelastic and elastic signals to determine the electron mean-free paths in the sample. Then, we converted these values to thicknesses in nanometers using reference mean free paths, corrected for our beam energy and collection and convergence angles using equation 5.2 in Reference 11. Then, using the bulk densities of Si and SiO$_2$, we converted areal densities of Si and O from EELS measurements into thicknesses. The measured values from EELS core-loss areal density measurements matched to within ~10% with thicknesses derived from low-loss thickness measurements.
9. Determinations of film thickness: FEFF simulations

Simulated EELS edges were generated using FEFF9 code, “an *ab initio* self-consistent multiple-scattering code… based on a real space Green’s function approach”\textsuperscript{13,14}. We input the 1- and 2-layer structures generated by the DFT relaxations in Section 12. For bulk SiO\textsubscript{2}, we used reference coordinates for α-quartz. The other parameters were: 60keV incident electrons with convergence and collection angles of 30 and 80 mrad, respectively, core-hole excitons included, and a 0.4 eV energy broadening. When structures contained atoms such as oxygen, which existed in multiple local chemical environments producing different edge shapes, the simulated edges were averaged weighted by their stoichiometry.

9. Determinations of film thickness: Images of silica edge

Another strong indication for bi-tetrahedral structure of the silica film was found at a flipped-over edge of the graphene where it was possible to image the silica film in side-view: Each graphene layer is clearly detectable as dark lines (3 layers in Supp. Figure 6a). According to the double layer silica film, two additional lines are detected in the covered areas as marked by the red arrows in Supp. Figure 6b.
To generate pair distribution functions, we used ImageJ to threshold and find the centroids of Si+O sites in ADF STEM images. These values were read into MATLAB, which we used to compute tables of in-plane nearest neighbor positions for each Si site. These lists were converted to radial distribution functions $f(r)$ by tabulating neighbor distances and dividing total counts by 2 to avoid double counting. We used 2D equivalents for definitions for the RDF of $f(r) = 2\pi r \rho(r)$ and PDF of $g(r) = \rho(r)/\rho_0$. Atom positions shorter than the nearest-neighbor Si-O-Si distances were chopped because these typically represented atoms in the center of rings, which we did not want to include in our distributions. EELS analysis of these center atoms revealed they were not Si atoms. Data intensities tail off at large radii because of the finite size of images.
11. Ring statistics

Ring sizes were tallied by hand from ADF images. Rings that appeared damaged or were difficult to identify were not counted. While the ring distributions of amorphous regions did not change significantly from region to region, the ratio of amorphous to crystalline rings varied considerably. To create the plots in Figure 5c-d, we had to choose a criterion to separate crystalline regions from amorphous ones. At these short length scales, the distinction is somewhat arbitrary. We chose to define crystalline regions as continuous groups of 6-membered rings that were 3x3 hexagons or larger with each hexagon oriented within a few degrees of the same direction. Some additional, interesting ring configurations are highlighted in Supp. Figure 7.

Supplemental Figure 7 | Catalog of interesting ring shapes. A few cropped images centering around rare or interesting shapes. The images are shown at different scales.

12. DFT structure and electronic simulations

In our first principles simulations we used the density-functional theory (DFT) as implemented in the plane-wave-basis-set VASP code\textsuperscript{15,16}. Projector augmented wave potentials\textsuperscript{17} were employed to describe the core electrons, and the generalized gradient approximation\textsuperscript{18} to describe the exchange and correlation. Kinetic energy cutoff for the plane waves was set to 500 eV, and all structures were relaxed until atomic forces were below 0.01 eV/Å. Brillouin zone sampling scheme of Monkhorst-Pack\textsuperscript{19} was used with a mesh of 15x15x1 to generate the k-points. A non-empirical functional\textsuperscript{20} for exchange and correlations, which is capable of describing both short-ranged covalent bonding and long-ranged van der Waals (vdW)-type interactions was used to simulate the graphene-silica systems. The nonlocal term in the vdW-DF was evaluated using the adaptive real-space approach\textsuperscript{21}. 

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Supplemental Figure 8 | Structural models and energetics of 2D silica-based crystalline nanosheets on graphene. a) Mono- and bi-tetrahedral structures considered for the 2D silica. b) Schematic illustrating DFT energetics calculations of the candidate structure. The bi-tetrahedral structure becomes energetically favored by 107 meV per structural unit over bulk SiO$_2$ when van der Waals (vdW) interaction with single-layer graphene is taken into account.

The SiO$_x$ structural models were constructed based on insights from the HRTEM images and their resemblance to the (001) projection of the β-tridymite structure of bulk silica, then the atomic positions and cell size were fully optimized. The reference energy for the bulk structure was that of the β-tridymite. To compare the energetics of systems with different chemical compositions, we used chemical potentials of H and O atoms as in an isolated H$_2$O molecule for mono-tetrahedral structures with a structural unit of Si$_2$O$_5$H$_2$. With these chemical potentials, the mono-tetrahedral structure was calculated to be slightly lower in energy than the bi-tetrahedral one (by ~94 meV and ~9 meV for the 'all-Up and 'Up-Down' configurations, respectively). After initial comparison, we checked how breaking the symmetry of the primitive unit cell affects the relaxation for larger supercells, and noticed that at least without the supporting graphene sheet, the mono-tetrahedral one structures were unstable, whereas the bi-tetrahedral structure remained stable in all of our calculations. Since the bi-tetrahedral structure is also a better match to the experimental TEM images, it is the most probable stable ultra-thin silica structure.

According to our DFT GGA calculations, the bi-tetrahedral structure has a hexagonal unit cell with a lattice constant of $a$=5.311 Å. The four silicon atoms are arranged in two layers with two atoms always along the same line in the z-direction, and one oxygen atom in between. The atoms within
the lower and upper silicon layers are further connected via oxygen atoms so that the structural unit is a Si-centered tetrahedron with oxygen atoms in each corner. The atomic positions are given in Supp. Table 1.

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Supplemental Table 1 | Atomic coordinates for the bi-tetrahedral structure. In the x and y-direction, relative coordinates are given, whereas the z-coordinate is given with an absolute value.

According to our electronic structure calculations with the DFT GGA method, the band structure of the bi-tetrahedral structure is very similar to that of bulk β-tridymite, as can be expected for an ionic material. The band structures are presented below along selected high symmetry lines.

Supplemental Figure 9 | Band structures of the bulk β-tridymite structure and the ultra-thin bi-tetrahedral silica as obtained within DFT GGA calculations.
Declaration

Herewith I declare that I wrote this doctoral thesis without external support and that I did not use other than quoted sources and auxiliary means. All statements which are literally or analogously taken from other than own publications, have been identified as quotations.

Ulm, March 2013 ..............................................

Simon Kurasch
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For invaluable microscope maintenance my thanks goes to Dr. Johannes Biskupek. Without your excellent, permanent efforts to keep the microscope up to date from both soft- and hardware side the microscope would not offer the excellent performance required for this edge-on research on a daily basis. This is very impressive, especially as you always have to fight against the ignorance and misusage of the relatively large group of operators. Hence, I’m specially grateful for your patience in teaching me various operation modes, tricks and workarounds. I’m very happy, that in addition we also had strong scientific interactions within the SALVE project.

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