Cutting and controlled modification of graphene with ion beams

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Abstract
Using atomistic computer simulations, we study how ion irradiation can be used to alter the morphology of a graphene monolayer, by introducing defects of specific type, and to cut graphene sheets. Based on the results of our analytical potential molecular dynamics simulations, a kinetic Monte Carlo code is developed for modeling morphological changes in a graphene monolayer under irradiation at macroscopic time scales. Impacts of He, Ne, Ar, Kr, Xe, and Ga ions with kinetic energies ranging from tens of eV to 10 MeV and angles of incidence between 0° and 88° are studied. Our results provide microscopic insights into the response of graphene to ion irradiation and can directly be used for the optimization of graphene cutting and patterning with focused ion beams.

1. Introduction
Recent reports on the large-scale production of graphene [1–3], including the growth of centimeter-size sheets on copper surfaces [4], have brought closer the utilization of graphene’s excellent electronic properties [5] in future electronic devices. In particular, quantum dots [6], nanoribbons [7], and antidot lattices [8, 9], which provide electron confinement within the graphene plane, have received considerable attention. Production of such structures is based on graphene patterning by various techniques such as electron beam lithography combined with reactive ion etching [6, 10, 11], chemical methods including unfolding of carbon nanotubes [12, 13], and graphene cutting with a focused electron beam [14].

Since focused ion beams (FIBs) are already routinely employed in today’s semiconductor industry, this method could become an alternative approach. Indeed, cutting and patterning graphene using a FIB with a high spatial resolution was recently demonstrated [15–17]. The method is based on using a 30 keV He ion beam in a helium ion microscope to directly sputter carbon atoms from predetermined areas of graphene sheets, either suspended or deposited on a substrate. Etched gaps down to 10 nm have been reported, with sharp edges and little evident damage or doping to the sample. Concurrently with the experiments on He beam-based patterning of graphene, the possibility of using Ar ion irradiation has also been studied [18].

Efficient use of ion beams and optimization of the graphene cutting process require detailed microscopic knowledge of damage production mechanisms and types of defects created by the energetic ions in the sample. In order to get an insight into the cutting process, the interaction of He ions with the target was modeled in [16] by a semi-empirical method [19] based on the binary-collision approximation, combined with statistical algorithms to calculate how a moving ion transfers its energy to the target atoms. This approach implemented in the trim software package [20] gives reasonable results for bulk materials. However, as has been pointed out [21, 22], the theory of irradiation effects developed for bulk materials does not always work at the nanoscale. In particular, it was recently demonstrated [23] that this approach cannot be applied to graphene, as the sample is treated as an amorphous matrix with a homogeneous mass density, while an explicit account of the atomic structure is required for atomically thin targets.

In this study, we use analytical potential (AP) molecular dynamics (MD) simulations, a much more accurate method than the one implemented in the trim code, to study defect production in graphene under ion irradiation. Our ultimate goal is to provide the means for determining optimum parameters,
such as ion mass, energy, and angle of incidence for graphene cutting, which would enable the production of smooth edges with the minimum number of defects at faster cutting rates. We simulated more than two million impacts of energetic ions onto suspended graphene and gathered statistics on types and abundances of defects for He, Ne, Ar, Kr, Xe, and Ga ions with energies ranging from tens of eV to 10 MeV. The role of the angle of incidence of the ions was studied in detail. To establish a direct link to the experiments, we further developed a kinetic Monte Carlo (kMC) code [24], which utilizes the statistics from the MD simulations for predicting the evolution of graphene under ion irradiation at macroscopic time scales. This allows modeling the behavior of irradiated graphene under realistic experimental conditions, e.g., in FIB systems.

2. Methods

In our MD simulations (a general introduction to this method can be found in [25]) the carbon–carbon interaction in graphene was modeled using the second-generation reactive empirical bond-order Brenner potential [26]. The bond conjugation term, which is not expected to be important in irradiation processes [27], was omitted. This approach has previously been successfully used in modeling the irradiation response of graphene and other carbon nanostructures [23, 28–31]. The interaction between energetic noble gas ions (He, Ne, Ar, Kr, and Xe) and target carbon atoms was simulated using the Ziegler–Biersack–Littmark universal repulsive potential [19]. In addition to the noble gas ions, irradiation with Ga ions was simulated using the same universal repulsive potential, as gallium is a typical ion species used in FIB systems. Chemical effects are expected to be important only at low ion energies (<250 eV) and they should not play any role at typical operating energies (∼30 keV) of FIB systems, especially in such a thin target, so that the use of the purely repulsive potential is justified also for the Ga–C interaction.

For a direct analogy with the experiments, we use the term ‘ion’ throughout this paper, although the charge of the incoming ion is not explicitly considered, as this is beyond the AP-MD method, and more importantly, the effects of low charge states are negligible [32]. The AP-MD approach is computationally efficient enough for running the massive number of simulations (more than two million runs in total) required to get statistically meaningful results in the large parameter space explored.

It is well known that electronic stopping is the main mechanism of energy transfer from an ion to any solid target at high ion energies [19]. At the same time, experiments [33, 34] indicate that energy deposited into electronic degrees of freedom of graphite gives rise to defects only if electronic stopping power exceeds a critical value of 7 keV nm⁻¹. Taking into account the excellent charge and heat conductance of graphene, similar behavior can be expected for this material [32]. As the typical electronic stopping value for all the ion/energy combinations used in our study is less than 0.7 keV nm⁻¹ (we calculated electronic stopping power using the approach of Ziegler et al [19]), and even the highest values for high energy Xe (∼4.5 keV nm⁻¹) are well below the critical one, electronic stopping effects were not taken into account.

The simulated graphene target consisted of 800 carbon atoms. Since thermal excitations due to temperature-related atomic motion do not play a significant role in the momentum transfer between the impinging ion and target atoms (typical phonon energies are within tens of meV per atom), the initial target temperature was chosen to be 0 K. After ion impacts the system was cooled down using the Berendsen thermostat [35] at the edges, with \( \Delta \tau = 10 \) fs as the time constant. Such a setup was used to model the dissipation of heat generated by the ion impact as would happen if the target was part of a larger graphene sheet. Additional simulations with the thermostat turned off showed, however, that the results are not sensitive to its parametrization, as the damage creation processes typically take place before the heat wave generated by the ion impact even reaches the system edges, barring a few cases in the high ion energy and high angle of incidence regime. Adaptive time step MD code parcas [36] was used for the simulations. Within the code, the simulation time step is dynamically adjusted based on the fastest moving particles in the system. This resulted in time steps ranging from the attosecond scale to close to 1 fs.

The system was allowed to relax for one picosecond after the ion impact. During this time the system had typically reached a local energy minimum. However, any reasonable simulation time is too short for the system to always find the most stable local configuration. To address this, the resulting structures were annealed for another picosecond at 1500 K and eventually cooled down to 0 K to facilitate further relaxation of the system and removal of at least the most unstable atomic configurations. Over macroscopic time scales at experimentally relevant temperatures (room temperature and above) the created defects are expected to reconstruct into patches of non-hexagonal carbon rings similar to those presented in [37]. Although the AP-MD method cannot capture the reconstruction processes, the sizes of these patches are defined by the initial damage which is statistically predicted by our results.

Impact points for the ions were chosen randomly within the minimum irreducible area of the graphene lattice. The direction of the incoming ion was determined by randomly selecting an inclination angle \( \theta \in [0°, 88°] \) and azimuthal angle \( \varphi \in [0°, 360°] \) independently so that for each \( \theta \) an average result could be generated over \( \varphi \). A schematic illustration of the simulation setup is presented in figure 1 along with an example of the effect of changing the \( \theta \) angle.

A link between the theoretical data on damage production and experiments can be provided within the framework of the kMC method. We have previously implemented such a model for comparing theoretical results with experiments in

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4 The set of simulated ion species (He, Ne, Ar, Kr, Xe, and Ga) was chosen to give a good representation of a large range of ion masses plus Ga as a special case, being a frequently used ion in FIB systems. The selection of ions in the code is being extended, and new ions and energies will be added once the calculations are completed.

5 The main principles of the molecular dynamics algorithms are presented in [43, 44]. The adaptive time step and electronic stopping algorithms are the same as in [45].
the cases of electron irradiation of carbon nanotubes [38] and hexagonal boron nitride monolayers [39]. Here, we developed a kMC model describing the response of graphene to ion irradiation by using the results from our AP-MD simulations as the source of damage event rates. Within this model, the impact event rate is derived from ion beam current, and the rates of producing any type of defects are derived by multiplying the ion impact rate by defect creation probability for the selected combination of ion species, irradiation energy, and angle of incidence. We employed data on the defect size (area initially covered by perfect hexagonal carbon rings transformed into other polygons, termed the ‘amorphized area’ within our kMC model) and the number of sputtered carbon atoms for each parameter combination. Because the MD simulations were always carried out on a pristine target, one should be careful when interpreting the kMC results when the defects start to overlap. However, as it is easier to displace under-coordinated atoms, our kMC results can be used to estimate the lower limit for the number of sputtered atoms even for overlapping defects.

3. Results and discussion

3.1. Dynamical simulations of defect production

When analyzing the results of the MD simulations, we categorized the defect structures produced in graphene into single vacancies (one missing atom from an otherwise intact structure), double vacancies (two missing atoms and no further damage), complex vacancies (defect structures with missing atoms other than single and double vacancies), and amorphous regions (defect structures with no missing atoms, the simplest example of such a structure being the Stone–Wales defect [40]). Experimental examples of these structures are presented in a recent review article [41], except for complex vacancies, examples of which are presented in [37]. We calculated the probabilities of producing each of these defect types for all ion species and the whole range of energies (35 eV–10 MeV) and angles of incidence (\( \theta \in [0^\circ, 88^\circ] \)) considered, as presented in figure 2. Also the probabilities of creating any defect were calculated.

As is evident from figure 2, varying any of the parameters has a drastic effect on the produced defect types and their abundances. At energies in the keV range, single vacancies are the typical defects when the angle of incidence is perpendicular to the graphene sheet. Upon tilting the ion beam, first double vacancies become the dominant defect type after which complex vacancies become the most common type of defect. This can be attributed to the increased projected density of graphene, when viewed from a grazing angle. The maxima in single vacancy production are shifted towards higher ion energies as the angle of incidence is increased, which can be useful when ion irradiation with a fixed energy is used for cutting graphene. The location of the maxima in complex vacancy production first moves toward lower energies with increasing angle of incidence after which it again moves to higher energies. Therefore, if graphene is to be used as a membrane in external beam experiments as suggested in [23], the resilience of the membrane can be improved by slightly tilting it. For example, in the case of 2 MeV Ne ions, tilting the graphene sheet by \( \sim 18^\circ \) will result in a twofold decrease in the sputtering rate, as will be discussed in more detail later in this paper.
A range of parameters where no defects are created corresponds to the large angle, low energy region of the graphs in figure 2. Low defect production has the same origin as ion channeling in crystalline solids. When coming in at a grazing angle, the ion interacts with a long row of atoms, and if the energy is low enough, depending on the angle of incidence, none of the target atoms receives enough momentum to be displaced. Instead, the ion is reflected away from the graphene sheet. However, if ion energy is increased, the ion will penetrate the sheet, and it typically creates significant damage along the way, as can be seen from the steeply rising complex vacancy probabilities in the low energy–large angle regimes in figure 2. Amorphization events are observed mostly at low ion energies ($\lesssim 1$ keV), where the ions have barely enough kinetic energy to displace a target atom, but the displaced atom remains bonded to the sheet as an adatom or a part of a local amorphization.

3.2. Statistical model for continuous defect production

General trends and dominant defect types for specific irradiation conditions can be directly obtained from figure 2. However, making quantitative predictions on the evolution of a graphene target under ion irradiation is not straightforward, as both variations in the defect sizes and the number of sputtered atoms must be taken into account. Also, the probability
Figure 3. Example results of kinetic Monte Carlo simulations of graphene evolution under ion irradiation. Blue (dark) circles mark single vacancies, whereas the red ones (light, with missing atoms) stand for other vacancy-type defects, and the green ones (light, no missing atoms) for amorphized areas with no missing atoms. Percentages of lost carbon atoms ($L$) and amorphized area ($A$) are given for each case. Note that vacancy-type defects also contribute to the percentage of amorphized area. All the numerical values were averaged over 25 simulations. The length of the scale bars is 5 nm in all the panels. The marked areas in panels (e) and (f) indicate the spot area of a focused ion beam limited at the full width at half maximum of the spot intensity. $\Phi$ is the irradiation fluence in ion impacts per unit area and dose stands for the total accumulated charge of the impinging ions.

distribution for creating each defect is not Gaussian, which means that the mean size and standard deviation are not sufficient for describing the damage caused to graphene. For this reason, we developed a kMC code, which directly uses the statistics on the sizes of the defects and number of sputtered atoms, extracted from the MD simulations. This code can be used for predicting the evolution of a graphene sheet under ion irradiation at macroscopic time scales. The code has a web-based interface [24] (see footnote 3) and is available for public use. Both a visual representation of the sample and quantitative estimates of the total amorphized area and the number of sputtered atoms can be obtained using the program. As the original data are collected for individual ion impacts on pristine graphene, we stress that the code underestimates the produced damage at high ion doses due to a drop in the displacement threshold energy for under-coordinated atoms [22].

To demonstrate the potential of the kMC code, in figures 3 and 4 we present example cases simulated with the code. If graphene is uniformly irradiated with 650 eV Ne ions at a normal direction to the sheet, a nearly exclusive production of single vacancies is observed (figure 3(a)). Changing the ion to 400 eV Kr will result in uniform distribution of single and double vacancies with roughly a 1/1 ratio (figure 3(b)). For high energy ions with incident direction normal to the sheet,
Figure 4. Results of kMC simulations of graphene evolution under ion irradiation with parametrization similar to that used in experiments in [15] (panel (a)) and with optimized irradiation angle with regard to cutting efficiency (panels (b) and (c)). Blue (dark) circles mark single vacancies, the red ones (light, with missing atoms) stand for other vacancy-type defects, and the green ones (light, no missing atoms) for amorphized areas with no missing atoms. The marked area indicates the area swept by the ion beam limited at the FWHM of the beam spot. Percentages of lost carbon atoms ($L$) and amorphized area ($A$) are given for each case. The scale bars are 5 nm. It is evident that by tilting the ion beam, the sputtering rate is increased significantly and the creation of local amorphizations is avoided. Line dose stands for the total accumulated charge through charged ion impacts per unit length.

The probability of creating any defect is greatly reduced, as is evident from figure 3(c) for the case of 2 MeV Ne: although the fluence is increased by one order of magnitude as compared to the previous examples, the total number of defects is lower. The individual defects are much larger, however, which can be attributed to the fact that during the interaction of a target atom and the fast ion the target atom is practically immobile, resulting in symmetrical momentum transfer in the direction of the ion trajectory. This leads to recoiled atoms moving very close to a direction perpendicular to the ion trajectory. In the case of ion trajectory perpendicular to the graphene sheet, this leads to in-plane collision cascades and large defect structures. This effect is also demonstrated in figure 1. If the direction of the ions is tilted away from the normal of the graphene plane, the typical direction of the recoiled atoms is correspondingly tilted out of the graphene plane, which results in smaller defect structures due to the absence of collision cascades, as can be seen in figure 3(d). Thus the resilience of graphene under high energy ion irradiation can be improved by tilting it, as was suggested above.
3.3. Optimizing ion beam cutting of graphene

As experimentally demonstrated by Lemme et al [15] and Pickard et al [17], a focused He ion beam can be used to cut graphene with a very high precision. The used acceleration voltage was 30 kV and the cutting was performed with the ion beam pointed in the normal direction of the sample surface. The effects of such irradiation on graphene are shown in figure 3(e) assuming a focused spot with a Gaussian distribution with a full width at half maximum (FWHM) of 6 nm. Approximately half of the damage events lead to sputtering of target atoms and half of the FWHM edge) is increased with the same total dose even though the spot area is larger. Also, as demonstrated previously, tilting the beam at high ion energies leads to decreased probability of creating in-plane collision cascades and local amorphizations, in favor of single vacancies. This leads ultimately to cleaner edges in cuts made with a FIB.

To further illustrate what can be achieved with parameter optimization when cutting graphene with a FIB, three examples of the use of the kMC code in linear scan mode are presented in figure 4. In these examples, the beam spot is moved in the vertical direction. The spot width is 10 nm (FWHM) and the beam direction is tilted towards the direction of the spot movement. The ion energy and species are similar to what was used in [15]. A line dose of 8 nC cm\(^{-1}\) was reported not to be adequate for making a cut in graphene. This observation is supported by our simulations (figure 4(a)): only \(\sim 6\%\) of the carbon atoms within the cut area are sputtered, although much of the area is amorphized. However, when the ion beam is tilted by 62.5\(^\circ\) there is almost a threefold increase in the number of sputtered atoms (figure 4(b)). To compare the effectiveness of graphene cutting at different angles of incidence, a third simulation was conducted, where the line dose was decreased so that the number of sputtered atoms is approximately the same as in the first case. Comparing the results in figures 4(a) and (c) shows that tilting the He beam by \(\sim 60^\circ\) gives a threefold increase in the cutting efficiency of the beam, while the amorphized area outside the cut is decreased considerably.

4. Conclusions

To conclude, we studied the effects of ion irradiation on graphene using atomistic computer simulations. The role of the angle of ion incidence in a wide range of energies was investigated, and the types and concentrations of defects were identified for various ions. The dramatic effect of the angle of incidence on defect production demonstrates the fundamental difference of strictly two-dimensional graphene from traditional bulk targets. The peculiarities of graphene’s response to ion irradiation can be used to gain detailed control over produced defect types and their abundances. The presented publicly available computer code [24] (see footnote 3) enables one to make quantitative predictions of defect production in graphene under energetic ion bombardment. This information is needed in order to controllably create specific types of defects, or when graphene is to be nanomachined by a FIB. To illustrate the latter, we showed an example where \(\sim 60^\circ\) tilting of the sample gave a threefold increase in sputtering and reduced the amorphized areas in the sample. Further on, with respect to the possible use of graphene membranes in ion beam analysis [23], we showed that the resilience of the membrane can be improved for high energy ions by choosing an optimum angle with regard to the direction of the ion beam. Although we looked specifically at noble gas irradiation, our results can also provide insights into the response of graphene to irradiation by other species, e.g. nitrogen, as in very recent experiments on irradiation mediated nitrogen doping of graphene [42].

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