Damage in graphene due to electronic excitation induced by highly charged ions

J Hopster1, R Kozubek1, B Ban-d’Etat2, S Guillous2, H Lebius2 and M Schleberger1

1 Fakultät für Physik and CeNIDE, Universität Duisburg-Essen, D-47048 Duisburg, Germany
2 CIMAP (CEA-CNRS-ENSICAEN-UCBN), F-14070 Caen Cedex 5, France
E-mail: marika.schleberger@uni-due.de

Received 16 November 2013, revised 10 February 2014
Accepted for publication 3 March 2014
Published 29 May 2014

Abstract
Graphene is expected to be rather insensitive to ion irradiation. We demonstrate that single layers of exfoliated graphene sustain significant damage from irradiation with slow highly charged ions. We have investigated the ion induced changes of graphene after irradiation with highly charged ions of different charge states ($q = 28–42$) and kinetic energies ($E_{kin} = 150–450$ keV). Atomic force microscopy images reveal that the ion induced defects are not topographic in nature but are related to a significant change in friction. To create these defects, a minimum charge state is needed. In addition to this threshold behaviour, the required minimum charge state as well as the defect diameter show a strong dependency on the kinetic energy of the projectiles. From the linear dependency of the defect diameter on the projectile velocity we infer that electronic excitations triggered by the incoming ion in the above-surface phase play a dominant role for this unexpected defect creation in graphene.

Keywords: graphene, ion irradiation, electronic excitation, scanning probe microscopy

One of the many amazing properties of graphene is its high resistance against irradiation damage. This is an advantage which can be exploited in novel applications such as transparent graphene windows [1] or graphene based radiation hard electronic and sensor devices [2–4]. On the other hand, this unique resilience limits the possibility, to use ion irradiation for modification purposes.

In principle, ion beams represent a very versatile tool for material modification, because they are easy to control with respect to energy and flux, they can be focussed and defocussed...
and are compatible with writing techniques as well as clean conditions. Most investigations about ion irradiation effects on graphene have been carried out with singly charged ions at low kinetic energies ([5–7], for a review see [8]), which create single and divacancies. Increasing the energy of the projectile does not change this—quite the contrary, the cross section for direct knock-on damage decreases drastically with energy [1]. Only with ion beams of extremely high kinetic energy (100 MeV and more) can graphene again be effectively damaged [3, 9, 10]. This is due to the fact that the energy loss mechanisms of these projectiles are entirely different. For very fast ions, knock-on damage is negligible, but instead ionization and intense excitation of the electronic system become dominant.

An elegant way to combine the advantages of both beam types, is the use of slow highly charged ions (HCI). In contrast to singly charged ions, HCI store a considerable amount of potential energy $E_{\text{pot}}$ (defined as the energy to remove the electrons from the initial atom to infinity). Therefore, they trigger significant electronic excitations in the near surface region upon impact, which can result in a variety of nanoscaled structural modifications [11]. Until now however, the response of graphene to this type of irradiation has not been investigated.

In this paper we show that highly charged ions can be applied to create significant modifications of graphene even by individual impacts. We demonstrate that HCI irradiation can be used to create regions of enhanced friction, which we attribute to chemical changes of the graphene lattice, and whose size can be easily controlled. We present evidence that this damage is due to the electronic excitation triggered by the projectile and that, in contrast to graphite, it only occurs above a certain potential energy, i.e. above a threshold $E_{\text{ph}}$. Furthermore, it turns out that the onset of defect formation in graphene as well as the defect size strongly depend on the ion’s kinetic energy. These findings suggest an entirely different defect creation mechanism as in the case of formerly investigated bulk materials.

Highly charged ion irradiations were performed at the Duisburg beamline HICS [12]. Xe$^{q+}$ ions with charge states $q = 28, 30, 32, 35, 38, 40$ and $42$ (covering a range of $E_{\text{pot}}$ from 12 to 45 keV) were used with the kinetic energy kept constant at $E_{\text{kin}} = 260$ keV. With fixed charge states 28 and 30, respectively, the kinetic energy was varied from 150 keV to 450 keV (partially performed at ARIBE at GANIL, Caen). The irradiation took place under perpendicular incidence with typical fluences of $1 \times 10^9$ ions cm$^{-2}$ resulting in non-overlapping impacts. High quality graphene samples were exfoliated from highly ordered pyrolytic graphite (HOPG) on 90 nm amorphous SiO$_2$ on Si, yielding single layer graphene (SLG) and thick few-layer graphene (FLG) flakes on the same sample enabling direct comparison. Characterization before irradiation included Raman spectroscopy for SLG verification and atomic force microscopy (AFM) operated in contact mode under ambient conditions. The unique shape of individual flakes enabled us to compare the exactly same region before and after irradiation. For detailed defect analysis the AFM was operated in friction force mode (FFM) [13], which is sensitive to friction changes. Particularly, regarding graphene, FFM allows the identification of graphene on different substrates [14], layer number and lattice orientation analysis [14, 15] as well as the observation of ripple structures [16].

After irradiation with varying charge states $q$, topography measurements by conventional contact mode revealed neither in SLG nor in FLG features that could be associated to ion irradiation. Only by using FFM, round defects were observed in the FFM friction signal, whose number corresponds very well with the ion fluence. Note that our fluences are by three orders of
magnitude lower as e.g. in [17, 18], so that we can exclude any effects from overlapping impact sites. We therefore conclude that each defect detected by FFM is related to a single ion impact. As an example we show the result of an ion irradiation experiment with Xe$^{38+}$ on SiO$_2$ supported graphene in figure 1. In the topography signal (a), SLG is barely visible due to its low height of nominally 3.95 Å. However, FFM can easily identify graphene layers by the contrast change in friction trace and retrace signals due to the different friction coefficients $\mu$ for graphene and SiO$_2$, respectively. Because torsion forces of the AFM cantilever lead to a linear deflection of the laser on the position sensitive detector, voltage values correspond qualitatively to friction forces. The sum of trace and retrace signals yields a topography induced friction signal [13], here shown in the lower part of figure 1(a). Accordingly, the half width of the trace/retrace loop represents the friction forces and is called a FFM-map (see figure 1(b)) in the following.

By comparing figures 1(a) and (b) a clear distinction between different materials, different graphene layers and other features is possible, as they show different friction values. A detailed analysis reveals a $\mu_{\text{SiO}_2}$ with twice the value of SLG (see figure 2(c)). For FLG, friction forces are somewhat lower than for SLG (b), in accordance with recent work [15]. The FFM map shows ion induced defects as point-like structures with a clearly enhanced friction compared to SLG. Averaging over 100 defects on SLG yields $\mu_{\text{defects}} \approx 1.5 \times \mu_{\text{SLG}}$ (see figure 2(d)). The diameter of the ion induced defects was determined by the full width at half maximum (FWHM) of gaussian fits to line scans taken in the FFM images (figures 2(a), (b)). The defect diameters appear to be quite large in comparison to the defects created by singly charged ions, which are known to create mainly single vacancies [19]. However, this is indeed typical for defect formation triggered by highly charged ions (see e.g. results from HCI irradiations of HOPG presented in [20, 21]) and already suggests that the origin of defect creation in SLG by HCI irradiation is not related to nuclear collisions. To rule out tip artefacts, we took with each new tip images from a reference sample (irradiated with $q = 35$ at 260 keV). From this image a scaling factor for that tip was determined by which the measured data could be calibrated against the reference. This method gives only relative numbers but ensures that any relative change in diameter will be detected independent on the individual tip shape or size, which

---

**Figure 1.** Scanning probe images of a SLG/SiO$_2$ sample irradiated with Xe$^{38+}$ and $E_{\text{kin}} = 260$ keV. Images were taken with 1 Hz scan speed and typical loading forces of a few nN. (a) Topography (upper part) and the topography induced friction (lower part). (b) Friction force map. (c) Optical microscope image (position of FFM images is marked) and Raman spectrum. The intensity ratio $I_{\text{sil}}/I_2 \approx 4$ and linewidth of $G$ peak FWHM (G) = 14.6 ± 0.3 cm$^{-1}$ are evidence for SLG.
would otherwise be needed to deconvolute the data. The mean defect diameter for all irradiated samples was then determined from gaussian fits to the respective diameter histograms. As an example, figure 2 shows diameter $d$ (FWHM) histograms of HCI induced defects on SLG after irradiation with $q = 30$ (a) and $q = 40$ (b).

The results for FLG and SLG for all charge states $q$ used in this study are compiled in figures 3(a) and (b). The error bars represent the FWHM of the gaussian. For both FLG (figure 3(a)) and SLG (figure 3(b)), there is a clear correlation between the diameter and the potential energy ($q$), i.e. a higher charge state $q$ yields an increased diameter $d$. A linear fit of the data for $E_{\text{kin}} = 260$ keV reveals a slope of $(0.21 \pm 0.04)$ nm keV$^{-1}$ for SLG and a lower slope of $(0.13 \pm 0.03)$ nm keV$^{-1}$ for FLG. In case of FLG, we could identify HCI induced defects after irradiation with every charge state used here, down to $q = 28$. Hence, no threshold behaviour is found for FLG. In contrast, for SLG (see figure 3(b)), the irradiation series with $E_{\text{kin}} = 260$ keV (solid squares) clearly shows a threshold behaviour with respect to potential energy. The threshold is between charge states $q = 28$ and 30, corresponding to potential energies of $12$ keV $< E_{\text{pth}} < 15.4$ keV. That is, a minimum potential energy $E_{\text{pth}}$ is necessary for defect formation in graphene. In addition, the threshold value varies with the kinetic energy as can be seen from figure 3(b). At higher kinetic energies $E_{\text{pth}}$ shifts to higher values, and to lower values at lower kinetic energies. The correlation between the diameter and the kinetic energy is equally apparent: for FLG (figure 3(a)) as well as for SLG (figure 3(b)), defect diameters increase with decreasing kinetic energy. Note however the distinct deviation between defect diameter in SLG and FLG at higher kinetic energies.

Figure 2. Histograms of defect diameters after irradiation with 260 keV Xe with (a) $q = 30$ and (b) $q = 40$, respectively. Histograms of friction coefficients for (c) pristine sample and (d) for defective areas (compiled from 100 individual impacts).
Let us first briefly discuss the FLG results. Due to our preparation technique via mechanical exfoliation from an HOPG crystal, we assume our FLG samples to be very similar to bulk HOPG samples. Our data should thus be comparable to recent results of Ritter et al. [20, 22], who reported HCI (Ar$^{9+}$ up to B$^{32+}$) induced defects on HOPG. In agreement with our data, they did not find a threshold, i.e. defects were created with potential energies as low as $E_{\text{pot}} = 0.99$ keV. No systematic influence of the charge state on the diameter of HCI-induced defects was reported. Here, we find a clear change in diameter as a function of the charge state. Intriguingly, the defects become larger when the projectile is slower. This could be related either to the time the projectile spends above the individual graphite layer and/or to the number of layers that is affected.

Next, we want to discuss the results obtained from HCI irradiated SLG. The threshold behaviour seen in figure 3(b) gives clear evidence that the potential energy deposited by the HCI is essential for defect creation. The kinetic energy can however not be neglected, as the
actual size of the affected area depends strongly on $E_{\text{kin}}$. This finding is in contrast to what has been observed in bulk alkali halides, alkaline earth halides and HOPG [22–25]. For CaF$_2$, the dependency of the structural surface modification on the charge state $q$ and the kinetic energy $E_{\text{kin}}$ of the projectile was investigated in great detail [23, 24] and could be explained in terms of different phase transitions and defect agglomeration mechanisms, respectively. The good agreement with model calculations based on a two-temperature-model [23] suggests, that the transfer of the primary electronic excitation to the lattice by electron–phonon-coupling is the origin of the structural modifications. In particular, they showed that the defect (hillocks) size does not depend significantly on the kinetic energy. We therefore propose that in the case of graphene an entirely different mechanism is triggered by the HCI impact, which will be discussed in the following.

With SLG (in contrast to HOPG) we can safely rule out effects from deeper graphite layers. To further exclude possible collisional or sputtering effects from the substrate as the origin of defect creation we repeated the experiment with freestanding SLG where we found basically the same type of defects. In addition, the SiO$_2$ substrates in our measurements did not show any significant defect formation upon HCI irradiation. We can thus directly conclude that for SLG the key factor for defect size must be the time, during which the projectile interacts with the graphene layer. A velocity plot reveals a linear dependency of $d$ on the velocity $v$ of the Xe$^{30+}$-ion (see figure 4). The linear fit to the data points of observed defects at $E_{\text{kin}} = 150–260$ keV can be extrapolated to higher velocities and predicts that no defects should be created at $E_{\text{kin}} = 450$ keV, which is in perfect agreement with our measured data. Because defect diameters in SLG and FLG increase with increasing $q$ at fixed $E_{\text{kin}}$, the defect formation must be driven by the potential energy deposition into the surface. From the observed decrease of $E_{\text{ph}}$ with decreasing $E_{\text{kin}}$ (see figure 3(b), $q = 28$ and $q = 30$ on SLG), we conclude that the available potential energy is deposited more efficiently by slower HCI. To fully describe the interaction of HCI with graphene we therefore have to take into account both forms of energy.

**Figure 4.** Diameters $d$ of HCI induced defects on SLG at $q = 30$ (taken from figure 3) as function of the velocity $v$ (for $E_{\text{kin}}$ see upper scale). A linear fit to data points for $150$ keV $\leq E_{\text{kin}} \leq 260$ keV was performed and extrapolated. The threshold prediction agrees well with our experimental findings.
deposition. For simplicity we neglect defect formation by nuclear collisions in the following as this has been shown to create mainly single and double vacancies [19].

In general, the HCI-solid interaction process can be separated into several stages [26, 27]. The first stage is usually explained in terms of the over-the-barrier model [28]. As the ion approaches the surface and passes a critical distance \( r_{\text{crit}} = \sqrt{2a/W_\phi} \) depending on the work function \( W_\phi \) of the respective material [29], it starts to neutralize by resonant electron capture and Auger ionisation. For SLG on \( \text{SiO}_2 \), the work function is typically 4.8 eV and this distance would thus yield \( r_{\text{crit}} \approx (2-3) \) nm for the charge states investigated here. During the neutralization phase, electrons from the target get caught into highly excited states of the projectile resulting in a so called hollow atom [30]. Deexcitation of this hollow atom starts in front of the surface and may continue via different Auger processes as well as collisional electron–electron processes. As a consequence, many excited electrons in the low energy range up to a few hundred eV as well as keV electrons due to Auger decay of unbalanced holes are created. The potential energy of each HCI results thus in a strong excitation of the electronic system as well as significant depletion of electrons of graphene within an area of only a few nm in diameter. This phase is directly related to the kinetic energy via the time of flight. The slower the ion, the more time it spends in this region resulting in an increased number of electrons emitted from graphene, provided the excitation processes take place on a time scale that is comparable with the time of interaction. Typical time scales for the above-surface processes are on the order of a few femtoseconds [31, 32] which is the same time a projectile with a few 100 keV in kinetic energy needs to overcome a distance of a nanometer. We therefore propose that the defect creation is governed mainly in the flight phase, within which the ion is neutralized by electrons supplied by graphene.

Finally, we address the nature of the defects. In principle there are several mechanisms by which these modifications could be created. The energy from the electronic system may be transferred via electron–phonon coupling to the lattice, resulting in a thermal spike [33] and possibly melting of the target [11]. This scenario works well for defect formation in various bulk targets [11, 24, 25, 34]. For graphene this scenario is questionable, as any form of electronic excitation should dissipate rapidly due to the high carrier mobility. Also, an inefficient electron–phonon-coupling on the order of \( 10^{13} \text{ J/(K \cdot s \cdot m)} \) [35] combined with the high thermal conductivity of graphene should prevent any structural modifications related to heating. Alternatively, the strong perturbation of the electronic system may result in direct removal of atoms via Coulomb repulsion or non-thermal melting [11]. To our knowledge there has been no clear evidence yet that either one of the latter two mechanisms can be triggered by HCI. A more likely mechanism is that the strong depletion of electrons in a localized area of SLG leads to a weakening or breaking of chemical bonds. The resulting dangling carbon bonds act as attractive adsorption sites for adatoms such as oxygen and hydrogen. This again will yield changes such as charge redistribution and rehybridization. Such chemically modified graphene will then give rise to an enhanced friction signal observable under ambient conditions [36, 37]. A quantitative comparison with our data is difficult due to different experimental parameters, but enhanced friction without topography enhancement clearly points towards chemically modified graphene [37]. We carried out additional investigations by optical spectroscopy and surface potential measurements which give clear evidence that the impact region indeed consists of hydrogenated graphene [38]. The size of such a modified area would be directly
related to the number of depleted electrons and, hence, for a given charge state to the velocity of the incoming ions. Further corroboration of this model is given by electron emission data on HCl impinging on HOPG [39]. As a crucial result, the electron emission yield $\gamma$ increases linearly with increasing $E_{pot}$ and decreases with increasing velocity, which is in excellent agreement with our data for $d(\nu)$, see figure 4.

To conclude, we showed that nanosized defective areas in SLG are induced by individual highly charged ions. The size of the defective area depends on the potential energy of the HCl and, surprisingly, on the kinetic energy as well. We propose that the significant depletion of electrons during HCl approach yields a breaking of graphene bonds followed by a saturation with other atoms. As a consequence the time of flight above the surface is the key parameter, by which defect size and threshold value are set. Defect creation in graphene by HCl can thus be controlled by a simple variation of kinetic energy (for a given and sufficiently high charge state). According to the extrapolation in figure 4, rather large defects with diameters of up to 20 nm could be created by using very slow HCl ($E_{kin}<1\text{ keV}$). This would also offer the chance to investigate the processes responsible for defect formation as well as the potential of defects for applications in much more detail. Apart from extending current limits, our approach to use highly charged ion beams offers a chance to address more fundamental issues such as radiation hardness of graphene devices or graphene’s response to intense electronic excitation.

Acknowledgments

This work has been financially supported by the DFG within the SFB 616: Energy dissipation at surfaces (JH) and the SPP 1459: Graphene (RK) as well as by the European Community as an Integrating Activity ‘Support of Public and Industrial Research Using Ion Beam Technology (SPIRIT)’ under EC contract no. 227012.

References

[1] Åhlgren E, Kotakoski J, Lehtinen O and Krasheninnikov A 2012 Appl. Phys. Lett. 100 233108
[2] Lopez J, Greer F and Greer J 2010 J. Appl. Phys. 107 104326
[3] Ochedowski O, Marinov K, Wilbs G, Keller G, Scheuschner N, Severin D, Bender M, Maultzsch J, Tegude F and Schleberger M 2013 J. Appl. Phys. 113 214306
[4] Zan R, Ramasse Q, Jalil R, Georgiou T, Bangert U and Novoselov K 2013 ACS Nano 7 10167–74
[5] Cancado L G, Jorio A, Ferreira E H M, Stavale F, Achete C A, Capaz R B, Moutinho M V O, Lombardo A, Kulmala T S and Ferrari A C 2011 Nano Lett. 1 3190
[6] Lucchese M, Stavale F, Ferreira E, Vilani C, Moutinho M, Capaz R, Achete C and Jorio A 2010 Carbon 48 1592
[7] Kalbac M, Lehtinen O, Krasheninnikov A V and Keinonen J 2013 Adv. Mater. 25 1004
[8] Krasheninnikov A V and Nordlund K 2010 J. Appl. Phys. 107 071301
[9] Akcöltekin S, Bukowska H, Peters T, Osmani O, Monnet I, Alzaher I, Ban-d’Etat B, Lebius H and Schleberger M 2010 Appl. Phys. Lett. 98 103103
[10] Ochedowski O, Kleine Bussmann B, Ban-d’Etat B, Lebius H and Schleberger M 2013 Appl. Phys. Lett. 102 153103
[11] Aumayr F, Facsko S, El-Said A S, Trautmann C and Schleberger M 2011 J. Phys.: Condens. Matter 23 393001
[12] Peters T, Haake C, Hopster J, Sokolovsky V, Wucher A and Schleberger M 2009 *Nucl. Instrum. Methods Phys. Res.* B **267** 687–90
[13] Grafström S, Ackermann J, Hagen T, Neumann R and Probst O 1994 *J. Vac. Sci. Technol.* B **12** 1559
[14] Marsden A J, Phillips M and Wilson N R 2013 *Nanotechnology* **24** 255704
[15] Lee C, Li Q, Kalb W, Liu X Z, Berger H, Carpick R W and Hone J 2010 *Science* **328** 76–80
[16] Choi J S *et al* 2011 *Science* **333** 607–10
[17] Compagnini G, Giannazzo F, Sonde S, Raineri V and Rimini E 2009 *Carbon* **47** 3201–7
[18] Giannazzo F, Sonde S, Raineri V and Rimini E 2009 *Appl. Phys. Lett.* **95** 263109
[19] Lehtinen O, Kotakoski J, Krasheninnikov A V, Tolvanen A, Nordlund K and Keinonen J 2010 *Phys. Rev.* B **81** 153401
[20] Ritter R *et al* 2010 *Nucl. Instrum. Methods Phys. Res.* B **268** 2897–900
[21] Nakamura N, Terada M, Nakai Y, Kanai Y, Ohtani S, Komaki K-I and Yamazaki Y 2005 SPM observation of nano-dots induced by slow highly charged ions *Nucl. Instrum. Methods Phys. Res. Sect.* B **232** 261–5
[22] Ritter R *et al* 2013 *Nucl. Instrum. Methods Phys. Res.* B **315** 252–6
[23] El-Said A S *et al* 2008 *Phys. Rev. Lett.* **100** 237601
[24] El-Said A S *et al* 2012 *Phys. Rev. Lett.* **109** 117602
[25] Heller R, Facsko S, Wilhelm R A and Möller W 2008 *Phys. Rev. Lett.* **101** 096102
[26] Arnau A *et al* 1997 *Surf. Sci. Rep.* **27** 113–239
[27] Schenkel T *et al* 1999 *Phys. Rev. Lett.* **83** 4273–6
[28] Burgdörfer J, Lerner P and Meyer F W 1991 *Phys. Rev.* A **44** 5674–85
[29] Winter H, Vana M, Lemell C and Aumayr F 1996 *Nucl. Instrum. Methods Phys. Res.* B **115** 224–32
[30] Briand J P *et al* 1990 *Phys. Rev. Lett.* **65** 159–62
[31] Winecki S, Cocke C L, Fry D and Stöckli M P 1996 *Phys. Rev.* A **53** 4228–37
[32] Burgdörfer J and Meyer F W 1993 *Phys. Rev.* A **47** 20–2
[33] Toulemonde M, Dufour C and Paumier E 1992 *Phys. Rev.* B **46** 14362–9
[34] Lake R E, Pomeroy J M, Grube H and Sosolik C E 2013 *Phys. Rev. Lett.* **107** 063202
[35] Fong K C and Schwab K C 2012 *Phys. Rev.* X **2** 031006
[36] Ko J H, Kwon S, Byun I S, Choi J S, Park B H, Kim Y H and Park J Y 2013 *Tribol. Lett.* **50** 137–44
[37] Byun I S *et al* 2011 *ACS Nano* **5** 6417–24
[38] Hopster J *et al* 2014 in preparation
[39] Wang Y *et al* 2011 *Chinese Phys. Lett.* **28** 053402