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Creating nanoporous graphene with swift heavy ions

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ABSTRACT

We examine swift heavy ion-induced defect production in suspended single layer graphene using Raman spectroscopy and a two temperature molecular dynamics model that couples the ionic and electronic subsystems. We show that an increase in the electronic stopping power of the ion results in an increase in the size of the pore-type defects, with a defect formation threshold at 1.22–1.48 keV/layer. We also report calculations of the specific electronic heat capacity of graphene with different chemical potentials and discuss the electronic thermal conductivity of graphene at high electronic temperatures, suggesting a value in the range of 1 Wm^{-1} K^{-1}. These results indicate that swift heavy ions can create nanopores in graphene, and that their size can be tuned between 1 and 4 nm diameter by choosing a suitable stopping power.

1. Introduction

Graphene has many attractive properties which have lead scientists to seek ways to apply this material. For example, it has been used in DNA sequencing [1], chemical sensing [2], gas separation [3–5] and water desalination [6]. Many of these applications require post-synthesis atomic scale modification of the material, which can not be accomplished by directly using the conventional methods without adapting them first for nanomaterials. For example, ion implantation of graphene requires energies several orders of magnitude lower than the conventional three-dimensional materials used in the semiconductor industry [7–11]. Also other types of modifications are possible with ion beams [12–16], but the effects depend sensitively on ion energy.

A rough division can be made between low energy ion irradiation (a few keV/nucleon) and high energy irradiation (a few hundreds of keV/nucleon). The ions in the latter energy range are referred to as swift heavy ions or SHI [17]. The lower energy ions slow down in materials via atomic collisions, whereas the high energy ions lose energy via interactions with the electronic subsystem, causing ionization and electronic excitations along the ion path. These channels of energy loss are characterized by nuclear (S_n) and electronic (S_e) stopping powers, respectively, and are expressed in units of energy loss/length.

Although many studies [18–23] have addressed the underlying mechanism of defect formation by SHI, these mechanisms still remain unclear. Several hypotheses have been proposed, such as Coulomb explosion [18,19], inelastic thermal spike [20,21], exciton self-trapping [22] and combinations of these [23,24]. Regardless of the underlying mechanism, it is well established that SHI tend to create structural modifications with cylindrical symmetry ('tracks') along the ion path within the target material [25].

Only a few experimental studies have addressed the effect of SHI irradiation in graphene [26–33]. Most of these experiments were performed on supported graphene and under oblique incidence.

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Measurement of SHI induced defects in single layers of suspended graphene under perpendicular incidence is still a challenge. During the experiments, the graphene samples become covered with hydrocarbon contaminants, which effectively prevent imaging of the defects under the contamination atoms. This makes it impossible to verify the pore-like nature of the irradiation-induced defects with imaging methods. Atomistic simulations can assist understanding of the processes that take place during irradiation. However, the model describing the interaction of ions with electrons in the simulations is of crucial importance, since it defines the dynamics of energy exchange between the electronic and ionic sublattices of graphene and hence is responsible for formation of final defects. In recent molecular dynamics simulations by Zhao and Jianming [16], the interaction of SHI with graphene was described by the inelastic thermal spike model [34–36], and the energy deposited on atoms by excited electrons was added instantaneously within a certain radius around the ion path. Although this model has proven sufficient for some cases in three-dimensional materials [34,37–41], in two-dimensional materials as graphene it is oversimplified, since it does not take into account the electronic subsystem and its energy exchange with the lattice during the simulation. Moreover, due to these simplifications, the model may fail to capture the key processes developing in a single layer material, leading to a strong uncertainty in the damage formation threshold, reported as 5.3–8 keV/nm (1.8–2.7 keV/layer) without validation from experiments.

In this study, we report a combined experimental and theoretical study of defect formation in suspended graphene by SHI ions. The induced defects are analyzed by Raman spectroscopy in combination with the two temperature molecular dynamics (TTMD) model [42], which couples the ionic and electronic subsystems in a concurrent multiscale simulation. This model was able to resolve inconsistency of experimental observations by SAXS and RBS measurements reported in Ref. [43] in contrast to the instantaneous thermal spike model [44]. In this study, we show that, assuming a constant electronic thermal conductivity of 1 Wm^{-1} K^{-1}, TTMD succeeds in reproducing the threshold for damage formation and the defect behaviour observed for graphene in two independent experiments. The good agreement between both experiments and the simulations establishes 1.22–1.48 keV/layer as the defect formation threshold in graphene.

2. Methods

2.1. Sample preparation and irradiation

We report the results of two independent experiments carried out on suspended single layer graphene samples. For clarity, we will refer to the results of our two different experiments as set A and set B. The graphene samples of set A were prepared using the mechanical exfoliation technique of a graphite crystal onto a patterned SiO_2/Si substrate. The pattern consisted of periodically etched holes in the sample with a diameter of 3.2 μm and a depth of about 8 μm. Graphene covering these holes is suspended (see Fig. 1 (a)). The layer thickness was checked by Raman spectroscopy using the FWHM of the 2*D* band [45]. In all samples, the disorder-induced *D* band was absent prior to irradiation. For the samples of set A, a linear background subtraction was applied. The samples of set B were commercially purchased. Graphene was grown by the chemical vapor deposition method [46] and transferred onto gold transmission electron microscopy grids with a porous carbon mesh by the provider. In this set, the size of the holes of the mesh (~ 1 μm) was close to the size of the laser beam, so that in most cases the recorded spectra contained a contribution of the *D* band. This background contribution was subtracted from the data presented in this work. For both sets A and B, the peaks were fitted with a combination of Gaussian and Lorentzian profiles with their spectral weight as a free parameter. Point spectra were taken from several different positions and then averaged. The error bars in Figs. 1 and 3 are the FWHM of the corresponding distribution.

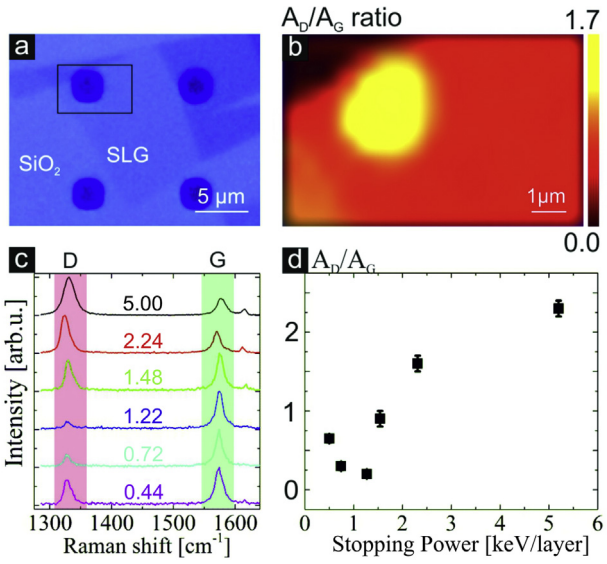

Fig. 1. (a) Optical image of a graphene flake exfoliated on a patterned SiO_2 substrate. (b) Raman mapping of the A_D/A_G peak area ratio of the box marked in the optical image. This sample was irradiated with 23 MeV I ions. The ratio is significantly enhanced for suspended graphene compared to SiO_2 supported graphene. (c) Some of the measured Raman spectra showing the evolution of the *D* (peaks marked in red) and the *G* (peaks marked in green) bands for different stopping powers in keV/layer. The fluence was 50.000 ions/μm^2. (d) The corresponding A_D/A_G peak area ratios plotted against the electronic stopping power of the SHI as calculated by SRIM. All results are shown for the graphene samples of set A (see text). (A colour version of this figure can be viewed online.)

The samples of set A were irradiated by SHI projectiles of varying kinetic energy at the IRRSUD beamline of GANIL (Caen, France) with 91 MeV Xe, at the Tandem van de Graaff accelerator of

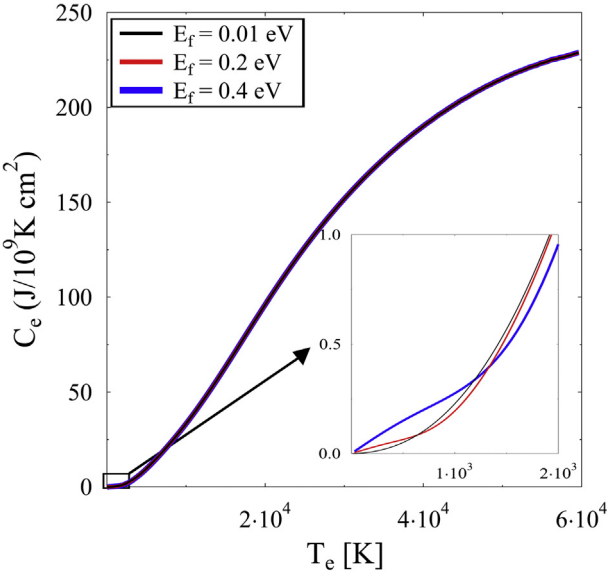

Fig. 2. (a) Electronic temperature dependence of the specific electronic heat capacity $C_e(T_e)$ of A-A stacked graphite for three different chemical potentials $E_F = 0.01$ eV, $E_F = 0.20$ eV and $E_F = 0.4$ eV. (A colour version of this figure can be viewed online.)