Electronic Supplementary Information

Understanding the Interaction between Energetic Ions and Freestanding Graphene towards Practical 2D Perforation

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Transferred Energy

The transferred energy to the target atom in the graphene strongly depends on the collision parameter p. Therefore one can calculate the amount of energy transferred to the C atom depending on a the area fraction $\gamma_A = p^2\pi/A_{graphene}$ of the graphene unit cell covered by p (**Figure S1**). Since energetic ions hit the graphene unit cell at a random location the area fraction can be identified with the fraction of C atoms hit the graphene target. As a result, one can estimate the percentage of C atoms gaining a certain transferred energy T. As an example ~50% of Ga^+ ions gaining more than the lattice displacement energy have energies higher than ~200eV compared to only ~15% in the case of He^+ (**Figure S1**).

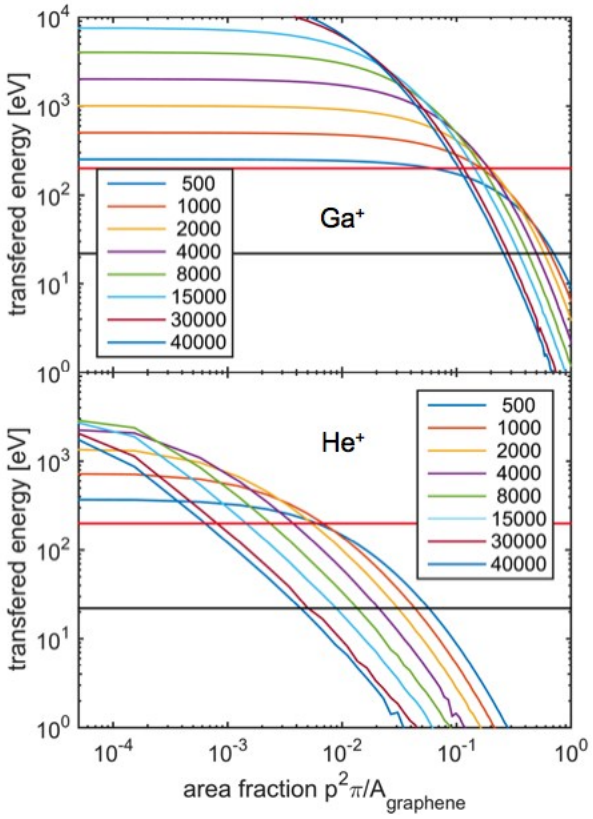

Figure S1. Transferred energy for Ga^+ and He^+ ion irradiation versus area fraction of the graphene unit covered by collision parameter p. Energy of incident ions given in eV. Two cutoff energies are displaced: black line corresponds to lattice displacement threshold of 23eV necessary to remove a C atom form the graphene lattice whereas the red solid line depicts the threshold line of 200 eV indicating the fraction of hit C atoms having significant recoiling energy.

Lower Bound of Theoretical Sputter Yield

The lower bound of the sputter yield can be derived by the following consideration. Initially the graphene sheet contains total number of carbon atoms, n_C. Each carbon atom has a scattering cross section area of A_C defined by the area in which the transferred energy of the ion hitting carbon atoms exceeds the lattice displacement energy E_L (see main text **Figure 1e** yellow area). The total scattering-cross-section area occupied by the carbon atoms meeting the sputtering condition equals to $n_C A_C$. Initially the probability of hitting a carbon atom, p_1, equals to the ratio of the total scattering-cross-section area to the total defined pattern area, A_t, yielding $p_1 = {n_C A_C}/{A_t}$. Once sputtering occurs in this event the number of carbon atoms is reduced by one, giving a new probability, $p_2 = {(n_C - 1)A_C}/{A_t}$, to the next carbon atom to be removed from the 2D lattice. By continuing this argument all the way to the rest of carbon atoms in the lattice, an average sputtering probability is obtained:

$$\bar{p} = \frac{n_C A_C/A_t + (n_C - 1)A_C/A_t + (n_C - 2)A_C/A_t + \ldots + (n_C - n_C + 1)A_C/A_t +}{n_C} = \frac{\sum_{i=1}^{n_C} i \, {A_C}/{A_t}}{n_C}.$$

Now noticing that ${A_C}/{A_t}$ is constant and that A_t can be expressed in number of initial carbon atoms n_C and unit cell area A_u ($A_t = {1}/{2 n_C A_u}$), one sees that ${A_C}/{A_t} = {1}/{n_C \gamma_U}$ contains the upper bound of sputter yield, γ_U. Therefore the mean probability can be rewritten as $\bar{p} = \frac{\sum_{i=1}^{n_C} i}{n_C^2}\gamma_U$. Noticing the summation over i, one immediately arrives at $\gamma_L = \frac{n_C + 1}{2 n_C}\gamma_U$.

Limiting Ion Beam induced deposition

On the He^+ FIB we used relatively high probe currents of 5-17 pA. These values are significantly higher than the standard imaging conditions and previously reported patterning currents of 0.5-1 pA.[15] However, we found the high probe currents to be necessary for large-scale graphene patterning because they enable to pattern 10^6 pores of sub-5 nm in size within 2 hours. For low currents we found out that dose required for the patterning increases substantially (by factor of 10-50). We attribute this increase to the

deposition of amorphous carbon material around the patterned area, which prevents readily removing of carbon atoms from the graphene lattice (**Figure S2a**).

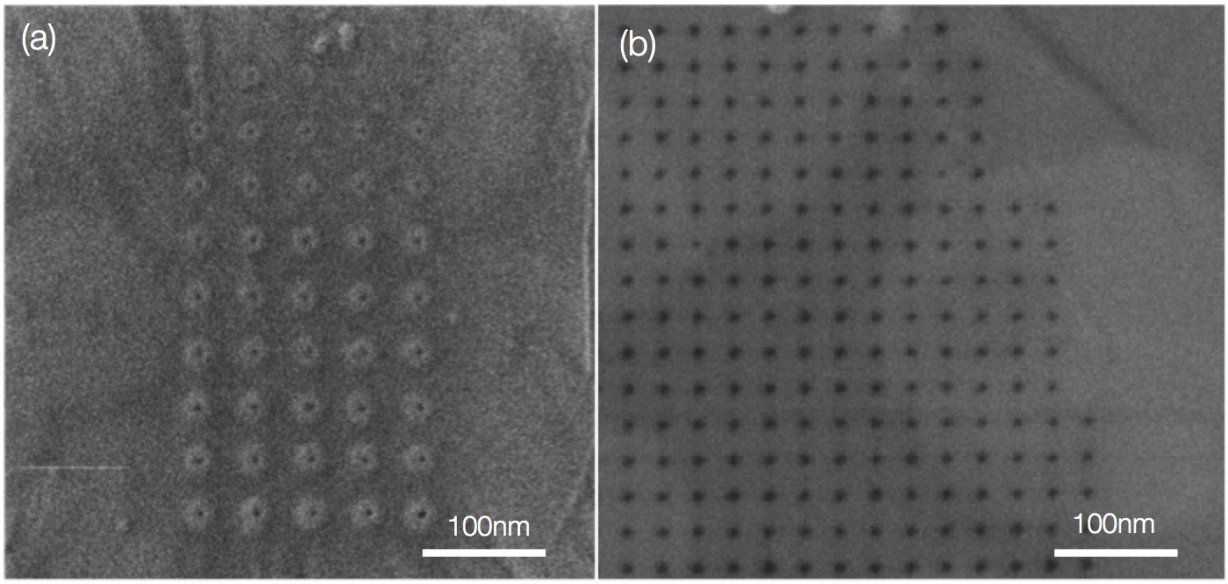

Figure S2. He^+ ion micrograph of etched pores in HIM. (**a**) Probe current of 1.4 pA and dwell times from 100 ms to 4600 ms (top to bottom row in steps of 500 ms). Strong deposition of material is visible around each patterned feature. Only beam-irradiation dwell times higher than 1600 ms show pores clearly visible in the micrograph. (**b**) Probe current of 10.5 pA with a dwell time of 15 ms leads to pore formation with no deposition in the vicinity of it.

Ion beam induced deposition is a widely reported phenomenon.[54] Gas molecules (e.g., volatile carbon species in the containing chamber) can adsorb on the target substrate, or the target substrate could already been contaminated by various adsorbates. When incident ions are inelastically scattered and create secondary electrons, these electrons can collide with and dissociate the adsorbates to leave nonvolatile compounds on the surface. This chemical reaction is limited by both the supply of adsorbing molecules as well as the reaction energy provided by the incoming ion flux. At low ion fluxes the contamination molecule mobility is high enough to move to the reaction site and build up material. In this case the reaction is limited by the energy input. This mechanism can be responsible for the deposition around the defined pattern (**Figure S2a**) and the very large dose values necessary to etch a hole onto graphene. At high ion fluxes the surface diffusion of the adsorbates to the patterning site is relatively slow, shifting the reaction toward a diffusion-limited regime. Using these patterning parameters

54. Utke, I.; Hoffmann, P.; Melngailis, J. *Journal of Vacuum Science & Technology B* **2008**, 26, 1197-1276.