SCALABLE NANOPATTERNING OF GRAPHENE BY HYDROGEN-PLASMA ETCHING

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EXECUTIVE SUMMARY

Scalable and precise nanopatterning of graphene is an essential step for graphene-based device fabrication. Hydrogen-plasma reactions have been shown to narrow graphene from the edges, or to selectively produce circular and hexagonal holes in the basal plane of graphene, but the underlying plasma-graphene chemistry is unknown. The petascale Blue Waters supercomputing resources have enabled us to quantify the mechanisms of hydrogen-plasma etching of graphene supported on SiO_2 substrate across the range of plasma ion energies. Specifically, our molecular dynamics simulation results, based on a reactive force-field potential, have uncover distinct etching mechanisms, operative within narrow ion energy windows, which explain the differing plasma-graphene reactions observed experimentally. These simulation results have provided rich insights into the complex plasma–graphene chemistry, opening up a means for controlled patterning of graphene.

RESEARCH CHALLENGE

The technique of plasma surface nanopatterning of materials has played an important role in the microfabrication over the past several decades of semiconductors of ever-reducing dimensions. Silicon, which has so far been the primary material for manufacturing of transistors, has reached its technological limitation with the recent 7-nm scale transistors. Use of novel materials such as graphene has been proposed in order to achieve the next milestone of the 5-nm ITRS node (International Technology Roadmap for Semiconductors). However, graphene has to be patterned to achieve its full potential in the domain of electronic applications. Several methods such as fluorination, boron nitride doping, irradiation by heavy ions, electron beam lithography and etching by hydrogen plasma have been used in the past for this purpose. Among these techniques, hydrogen plasma etching has shown the most promise in terms of scalability and cost effectiveness. While there exists ample experimental evidence for the pattering of graphene by hydrogen-plasma treatment, the reported etching reactions and the resulting graphene nanostructures have been vastly different. These reactions range from selective edge etching with no damage to its basal plane, to combined basal plane and edge etching of graphene resulting in isotropic and anisotropic hole growth in the basal plane of graphene. To date, controlling the patterned graphene nanostructures by hydrogen-plasma treatment has not been achieved due to a lack of fundamental understanding of the complex hydrogen plasma-graphene chemistry. Furthermore, the complete parameter space of substrate temperature, ion energy, and incident flux has not been systematically studied due to the cost limitations of plasma experiments.

METHODS AND CODES

We perform length-scale bridging by delineating the contributions of the edge and basal plane etching using ReaxFF-based molecular dynamics (MD) and linking these processes together via a mechanistic model. All our simulations were performed on the C++-based open source LAMMPS code.

RESULTS & IMPACT

We quantify the extent of basal plane damage for each ion energy by defining a damage parameter D_b as the fraction of broken C–C bonds in the graphene sheet. The basal plane of graphene remains nearly undamaged at ion energies of 1 eV and 25 eV, but displays a nonmonotonous relationship with ion energies in between. Peak etching is observed at ion energy of 10 eV, as shown in Fig. 1a. The basal-plane etching initiates with the chemisorption of the H atoms on two neighboring C atoms and proceeds with the further hydrogenation of the dangling C–C bonds, as shown in Fig. 1b. To quantify the edge-etching of graphene, we define an edge-etching rate D_e and measure its variation with ion energy and for both zigzag and armchair orientations, as shown in Fig. 1c. Our results demonstrate distinct ion energy regimes for isotropic versus anisotropic etching. Between 1 and 5 eV, the average armchair and zigzag etching rates are similar with overlapping error bars. At ion energies of between 7 and 30 eV, however, armchair etching consistently proceeds faster than zigzag etching by ~15%, suggesting that the patterned holes should indeed be hexagonal with zigzag-oriented edge structures, in agreement with experimental observations. Fig. 1d shows the mechanisms of etching at the zigzag and armchair edge. H-induced etching as well as direct impact damage plays a role in zigzag edge, while only the latter is active in the more stable armchair edge. These distinctive etching mechanisms, which are operative within narrow ion energy regimes, fully explain the differing plasma-graphene reactions observed experimentally.

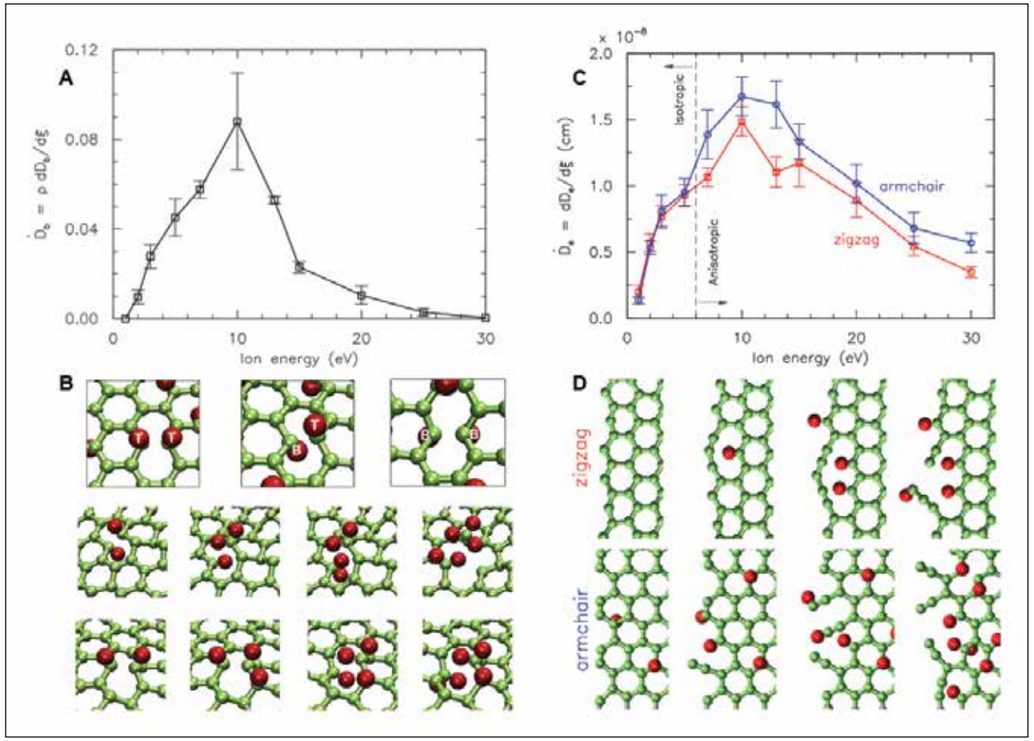

Figure 1: a) Steady state basal plane etching rate versus ion energy for monolayer graphene; b) Mechanism of etching showing the three possible configurations of damage nucleation and progression; c) Etching rates of the zigzag and armchair configurations versus ion energy; and d) Mechanism of etching for zigzag and armchair edges.

WHY BLUE WATERS

The Blue Waters computational capacities were necessary for several reasons. First, the complex chemistry and plasma surface interactions involved in the hydrogen etching of graphene require the use of fully reactive MD potential, allowing for potential reactions between the Si, O, C, and H species at each MD time step. Second, the impact dynamics of impinging H atoms on graphene requires the use of a small time step (0.15 fs), which further increases computational cost. Third, studying the edges of the multilayer graphene presents a wide range of possible configurations, as the edges can be partially or completely covered by a graphene layer. Finally, because of the random process of H deposition, a large number of simulation runs are required to obtain statistically significant findings.

PUBLICATIONS AND DATA SETS

Harpale, A., and H. B. Chew, Hydrogen-plasma patterning of multilayer graphene: Mechanisms and modeling. *Carbon*, 117 (2017), DOI: 10.1016/j.carbon.2017.02.062

Harpale, A., M. Panesi, and H. B. Chew, Plasma-graphene interaction and its effects on nanoscale patterning. Phys. Rev. B, 93 (2016), DOI: 10.1103/*PhysRevB*.93.035416