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Hydrogen-plasma patterning of multilayer graphene: Mechanisms and modeling

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A B S T R A C T

We study the atomic-scale etching mechanisms of multilayer graphene, and the subsequent formation of nanopores, when exposed to downstream hydrogen plasma. Our molecular dynamics simulations based on reactive force-field potential reveal precise energy regimes for the transport of ions through, and selective etching of, individual graphene layers within the multilayer structure. Etching initiates with hydrogenation of the graphene basal plane, followed by localized C–C bond breaking which leads to the formation of CH_2, and subsequently, unstable CH_3 bond configurations. We establish the basal plane and edge etching rates of the individual graphene layers as a function of ion energy, and introduce a micromechanics model to predict the 3D-patterned pore structure at experimental length- and time-scales. Our results demonstrate the development of columnar holes in multilayered graphene, which transition to stepped-edge holes at higher fluence due to cumulative effects of basal-plane etching. The contributions of thermal radicals and dehydrogenation effects on the hole growth process are discussed.

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1. Introduction

Graphene is one of the most promising nanomaterials because of its novel mechanical, electrical, thermal, and optical properties [1,2]. Current chemical vapor deposition methods are able to fabricate high-quality, macroscopic-scale graphene sheets cheaply and in large quantities [3–6]. However, most of graphene's potential applications, ranging from engineering to medicine, require pattering of graphene. For example, the etching of graphene from the edges to form nanoribbons or the patterning of holes in the basal plane of graphene can open a bandgap to enable graphene electronics [7,8]; nanoporous graphene is also used for DNA sequencing, gas filtration, and water desalination [9–11].

One attractive scalable approach for functionalizing and patterning monolayer and multilayer graphene is by hydrogen plasma treatment. In a typical setup, H_2 gas is pumped at low pressures into an RF plasma chamber, producing atomic H radicals and a mixture of ions (H^+, H_2^+, and H_3^+) which react with graphene on SiO_2 substrates placed downstream of the discharge [12]. The H radicals have a density 10–100 times that of the ions, but these thermal radicals cannot hydrogenate the pristine graphene basal plane [13,14]. In contrast, the ions are accelerated through the plasma sheath, and bombard the graphene surface. Energy-filtered mass spectroscopy measurements show that H_3^+ ions are 100 times denser than the H_2^+ and H^+ ions, and can reach ion energies of up to ~45 eV near the downstream graphene surface, depending on plasma characteristics such as power, pressure, and downstream position [12].

Three distinct mechanisms have been observed in the hydrogen-plasma etching of monolayer graphene: (a) selective narrowing of graphene from the edges with no damage to the basal plane resulting in graphene nanoribbons [15], and combined edge and basal plane etching to form either (b) circular holes [16] or (c) hexagonal holes [17] in the graphene basal plane. Our previous molecular dynamics (MD) simulations on the hydrogen-plasma etching of monolayer graphene reveal specific H ion energy windows resulting in mechanisms (a)-(c): the ions have sufficient energy to react only with the graphene edges to cause selective edge-etching at low ion energies of ~1 eV, but can hydrogenate the basal plane and initiate basal-plane etching at higher ion energies. The simulations also reveal a sharp transition from isotropic to anisotropic edge-etching at ~5 eV, which explains the circular or hexagonal hole patterns reported in differing experiments for monolayer graphene [18]. The hydrogen-plasma etching reactions are surprisingly different for multilayer graphene. Some have reported roughening and blister formation on the surface of multilayer

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graphene but with no visible etch pits [19,20]. Others have demonstrated 2D patterns of hexagonal columnar holes or 3D patterns of hexagonal stepped-edge holes in the basal plane of multilayer graphene and HOPG [16,17]. However, the formation of circular holes was never reported for multilayer graphene, even when the experimental conditions were identical to those resulting in circular holes for monolayer graphene. In addition, the edge-etching and hole growth rates for multilayer graphene were approximately three times slower than for monolayer graphene [15–17].

In this work, we study the early-stages of hydrogen-plasma etching of multilayer graphene, across ion energy levels of 2–40 eV, using MD simulations based on reactive force-field (ReaxFF) potential. We uncover narrow energy regimes for ion transmission to achieve targeted etching of the individual graphene layers within the multilayer structure. The etching rates obtained from MD are scaled to experimental length- and time-scales via a mechanistic model which incorporates the added contributions of hydrogen radicals and dehydrogenation effects. Our model predicts a transition in the hole growth pattern from columnar to stepped-edge type, which explains the etching patterns observed experimentally in multilayer graphene.

2. Computational methods

The plasma-etching of graphene is caused by the energetic bombardment of H^+, H_2^+, and H_3^+ ions with energies of up to ~45 eV. Regardless of the ion type, these energetic ions undergo dissociative recombination to form neutral, but energetic, H radicals near the graphene surface. For example, two possible branching reactions for the most prevalent ion type, H_3^+, are $H_3^+ + e \rightarrow H_2 + H$ or 3H [21,22]. Here, we directly simulate the energetic bombardment of H atoms on quad-layer graphene supported on SiO_2 substrate (Fig. 1a). Our MD simulations are performed using LAMMPS [23]. The atomic interactions between the Si, O, H, and C atoms are fully-governed by a reactive-force-field (ReaxFF) potential which consists of bond-order-dependent valence terms, position-dependent charge distribution, and non-bonded van der Waals and Columbic interactions. This potential allows for continuous bond breaking and reforming, and potential chemical and physical reactions involving the SiO_2 substrate [24,25]. We have previously performed a series of validation studies to show that this potential accurately captures the activation barrier and formation energies for hydrogenation of graphene [18]. The associated sp^2 to sp^3 transitions in the hybridization state and local deformations in the bonding structure were also found to be in good agreement with prior DFT studies [26–28].

Our MD simulations comprise of a 1.1 nm thick α quartz SiO_2 substrate which is oxygen terminated and with the (001) plane oriented normal to the vertical (z) axis (Fig. 1b). An ABA-stacked, quad-layer graphene sheet is modeled above the SiO_2 substrate, and the individual graphene layers are labeled L_1 to L_4 sequentially from the top (Fig. 1a). Our graphene-SiO_2 system is periodic in the in-plane (x-y) directions. The $11.1 \times 10.8 \times 6.1$ nm^3 dimensions of the MD simulation box are chosen to minimize the lattice mismatch strain between graphene and SiO_2 (~0.07%). We fix the bottom 0.5 nm thick slab of SiO_2 atoms throughout our simulations, and designate the next 0.5 nm thick slab above as the heat bath. All of our simulations are conducted with a time step of 0.15 fs. Prior to initiating the bombardment sequence, we subject the graphene-SiO_2 system to an NVT ensemble maintained at a temperature of 300 °C by a Berendsen thermostat for 1.5 ps; this temperature is typical of plasma-graphene etching experiments [16–18]. Throughout our simulations, the graphene layers maintain their ABA stacking configurations with interlayer spacing of ~0.34 nm which corresponds to that of HOPG.
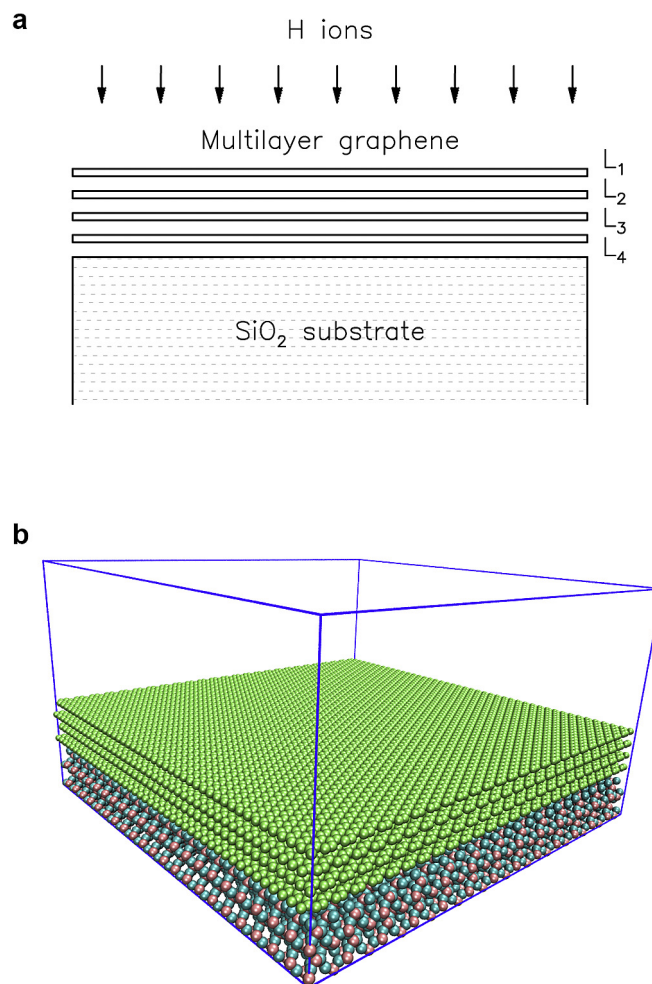

Fig. 1. (a) Schematic of the energetic bombardment of H ions on quad-layer graphene supported on SiO_2 substrate; individual graphene layers labeled L_1 to L_4 sequentially from the top. (b) Initial atomic configuration of a quad-layer graphene sheet on SiO_2. The C, Si, and O atoms are colored in green, pink, and cyan, respectively. The MD simulation box, outlined in blue, is periodic in the in-plane directions. (A colour version of this figure can be viewed online.)

We divide the in-plane dimensions of the MD simulation box into 4 by 4 grids and simultaneously deposit one H atom per grid (16 in total) randomly from 0.6 nm above the top graphene layer L_1; each H atom has initial velocity in the $-z$ direction corresponding to kinetic energy of 2–40 eV. Because of the relatively large in-plane dimensions of the simulation box, each of the 16 impact locations on the multilayer graphene sheet are sufficiently separated and can be considered as independent events. After initiating this deposition process, we equilibrate the entire system without a thermostat for the first 0.9 ps to resolve the initial impact dynamics. Thereafter, we switch on the thermostat in the heat-bath region and set it to the target temperature of 300 °C for the next 2.4 ps, before quenching the graphene sheet to 300 °C for 0.3 ps. The entire bombardment sequence is then repeated for the next 16 H atom impacts. This choice of the 3.6-ps bombardment cycle period allows us to time accelerate the etching process to simulate over 225 bombardment cycles (3600 H atom impacts), which effectively represents a fluence of $\sim 3.0 \times 10^{15}$ ions/cm^2. This time-accelerated approach, however, considers only the contribution of energetic H ions to the etching process and cannot account for longer-time-scale events, specifically, the effects of hydrogen radicals and temperature-induced dehydrogenation. These longer