Evolution of carbon surfaces under simulated bombardment by deuterium

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Abstract. The bombardment of both graphite and deuterated amorphous carbon surfaces with 20 eV D atoms has been performed using molecular dynamics simulation. The primary purpose of these simulations is to determine whether the eventual state of the surface, once it has reached a steady state, is independent of the starting structure. It is found that while independently realized amorphous carbon structures give rise to similar impact-modified surfaces, the graphitic surface evolves towards a somewhat different structure. Including or neglecting a realistic treatment of the nonbonded interactions in the graphite bombardment does not result in large differences in the impact-modified structure, although the penetration depth is considerably less when nonbonded interactions are included.

1. Introduction
Ion-surface collisions are relevant to a wide variety of scientific and technological applications, ranging from astrophysical systems to surface analytical methods and plasma-surface interactions. In particular, impact of hydrogen, especially its heavy isotopes, on carbon-based materials is of relevance for magnetically confined hydrogen fusion plasmas, in which graphitic materials are often used as plasma-facing components, due to their advantageous thermal and mechanical properties, as well as their low atomic number. Consequently, there has been a great deal of interest in the sputtering of graphite and amorphous carbon by atomic, ionic, and molecular hydrogen isotopes, much of it at the chemical sputtering energy range of between 5 and \(\sim 100\) eV.\cite{1–3} Previous work has included both experimental\cite{2–8} and computational\cite{6–20} approaches, using both monoenergetic beams and plasmas.

One key observation that arises from recent comparisons between simulation and experiment is the importance of surface treatment.\cite{6–8} The sputtering takes place at a surface that has been modified by interactions with the beam or plasma, and is highly dependent on this modified surface structure. Thus, early simulations bombarded surfaces such as hydrogenated amorphous carbon (a-C:H), typically constructed by heating and annealing a randomly constructed surface in an attempt to mimic a beam- or plasma-modified surface.\cite{6; 9; 10} More recent simulations, however, have discovered that the surface composition and morphology are very sensitive to the bombardment conditions, and that structural and sputtering properties are dramatically different for a worn-in surface than for as-constructed amorphous surfaces that have experienced no impacts.\cite{11–16} The current understanding is that each particular set of beam or plasma...
conditions drives the surface composition towards a unique steady state composition, and that sputtering simulations must be performed on a carefully prepared steady-state surface which mimics all experimental parameters in order to reproduce experimental results. We here define a steady state hypothesis which assumes that the steady state depends on the bombardment conditions, but is independent of the initial state of the surface from which it evolves. The former assumption has been verified many times: the worn-in surface structure clearly varies with different impact conditions.[13–20] However, the latter assumption — that different initial surfaces will (eventually) evolve towards similar steady state compositions under identical bombardment conditions — has been tested only for structurally similar surfaces, such as independent realizations of a-C:H. The validity of this assumption determines whether it is necessary to reproduce the exact initial surface structure in order to model a specific experiment, or whether it is acceptable to begin with an initial surface such as a-C:H that is already similar to the expected steady state.[7; 13; 16] The purpose of the current work is to examine this question in some detail, by investigating the evolution of the surface towards an eventual steady state for more chemically dissimilar initial states: crystalline graphite and a-C:H.

2. Computational Methods
In the simulations performed here, systems of both deuterated amorphous carbon (a-C:D) and graphite were bombarded by deuterium atoms, and the resulting dynamics were studied by molecular dynamics with two different potential models. The graphite system comprised 1440 atoms in eight layers. Periodic boundary conditions were imposed in the two Cartesian dimensions parallel to the graphite layers, with box lengths of 22.151 Å and 21.315 Å. The graphite layers were initially separated by 3.35 Å, resulting in a system size of 23.45 Å in the direction perpendicular to the graphite layers, which we label z. The system size was free to change in this direction, as periodic boundary conditions were not applied in this dimension. An a-C:D system consisting of 1750 C atoms and 750 D atoms was constructed as in previous work[12; 13] by quenching a high-temperature system constructed with a D:C ratio of 0.4. As with the graphite system, periodic boundary conditions are imposed only in the x and y dimensions, each with length 26.506 Å. Two independent a-C:D systems were constructed with the same procedure, for use in determining the effect of small statistical differences in surface structure. The graphite and a-C:D systems were all equilibrated at 750 K using a Langevin thermostat before beginning bombardment.

All three simulations were performed with the REBO potential, which is able to treat covalent bonding interactions in hydrocarbon systems, and was originally developed for chemical vapor deposition.[21; 22] The REBO potential does not include any treatment of nonbonded interactions, such as dispersion and exchange repulsion, both of which are important in order to model the graphite system accurately. Consequently, the bombardment of the graphite system was also modeled independently with the AIREBO potential, which is an extension of the REBO potential to include these nonbonded interactions.[23] Most previous simulations of sputtering of a-C:H have been performed with the computationally less expensive REBO potential, with the assumption that nonbonded interactions are generally negligible in network solids such as a-C:H at impact energies above the sputtering threshold.[6; 9; 11–16; 18; 20] A few previous simulations have used AIREBO,[10; 17] although none have examined the effect of the potential on surface modification. Thus, we bombarded four systems in total: graphite and two independent a-C:D surfaces with REBO, and graphite with AIREBO.

The bombardment was performed by introducing a D atom at least 12 Å above the surface, at a random lateral position, with a kinetic energy of 20 eV directed normal to the surface. The surface was allowed to evolve freely for 2.0 ps after the impact, after which point a Langevin thermostat with a target temperature of 750 K and a time constant of 100 fs was applied to the surface for another 2.0 ps in order to remove the deposited thermal energy. During the 2.0 ps
of unconstrained dynamics, the molecular dynamics used a variable-timestep integrator.[24] Allowing the integration timestep to change during the simulation is important for sputtering simulations, as the very small timesteps that are needed for adequate energy conservation during the collision cascade would be extremely inefficient when modeling merely thermal motion. The average timestep during the early phases of the collision was \(\sim 0.001\) fs, while the timestep rose to \(\sim 0.2\) fs in the second ps after the impact. During the thermostatted portion of the dynamics, a constant timestep of 0.25 fs was used.

In order to keep the impacts from imparting any net momentum to the substrate, a portion of the system farthest from the impact interface was constrained to have a fixed position in the \(z\) dimension during the dynamics (these atoms were unconstrained in the dimensions parallel to the interface); this portion of the surface consisted of either one layer of graphite, or the lowermost 3.35 Å of atoms in the a-C:D systems.

Because the REBO potential does not include any attractive interaction between graphite layers, a single atom in each graphite layer was constrained to remain at a fixed \(z\) position; without this constraint, the momentum imparted to the surface by the impact would occasionally (and unphysically) result in exfoliation of one or more graphite layers. These fixed-atom constraints were removed, one at a time, as soon as a crosslink was formed between the constrained layer and the one beneath it. The number of degrees of freedom used in calculating the instantaneous temperature accounted correctly for the number of constraints at all times.

Because there were 4.0 ps of dynamics between impacts, the nominal flux at which the bombardment was performed was \(3.6 \times 10^{28}\) D m\(^{-2}\) s\(^{-1}\) for a-C:D and \(5.3 \times 10^{28}\) D m\(^{-2}\) s\(^{-1}\) for graphite. This is many orders of magnitude larger than experimental fluences, which will only reach \(\sim 10^{20}\) D m\(^{-2}\) s\(^{-1}\) even in large fusion reactors such as ITER. The effective flux is much lower, however, because the 2.0 ps thermostating phase serves to remove the excess thermal energy that would be dissipated in the \(\mu\)s or ms between local impacts at experimental fluxes. Although we are able to model the very fast collision dynamics, as well as account for the slow thermal transport in an effective way, it is important to note that there are slow kinetic effects, such as diffusion of mobile defects, that will not occur at molecular dynamics timescales.

Each surface was bombarded sequentially by between 700 and 1700 D impacts, reaching total fluences of up to \(3.5 \times 10^{20}\) D m\(^{-2}\) for the graphite REBO system. Any reflected or sputtered species were removed from the simulation once they were more than 30 Å from the interface with a center-of-mass velocity directed away from the surface; the position of this interface was adjusted to account for swelling of the substrate, so that particles were only removed once they were no longer interacting with the substrate.

3. Results and Discussion

To illustrate the evolution of the surface under bombardment, we first examine the behavior of the a-C:H surface under bombardment by 20 eV D atoms at normal incidence, using the REBO potential. This particular combination of surface, potential, and bombardment conditions has been studied previously,[7; 11; 13; 14; 16; 17] although at a surface temperature of 300 K rather than 750 K. Analysis of this system, in comparison with previous results, may thus yield insights into the anomalously high sputter yields at temperatures near 750 K,[1] a phenomenon that is not yet fully understood. The emphasis here, however, is on structural properties, rather than sputter yields. Figure 1 shows how the density of both C and D atoms evolves in this system with increasing fluence.

In the initial, as-prepared surface (at zero fluence), the C and D densities exhibit random fluctuations due to the finite sample size, but the average density is independent of distance from the interface. The surface composition changes, however, under bombardment, with a decrease in C density due to erosion and an increase in D density due to implantation. The 20 eV D atoms modify the surface to approximately 15 Å beneath the interface, and the D:C ratio in this
Figure 1. Evolution of carbon density (left panel) and hydrogen density (right panel) in a deuterated amorphous carbon surface under bombardment by 20 eV D atoms, simulated with the REBO potential, at fluences indicated in the legend in units of $10^{20}$ D m$^{-2}$.

The graphite surface was bombarded using the REBO potential in an effort to determine whether a different initial surface would approach the same steady state under identical bombardment conditions. This is an important comparison, since the carbon-containing plasma-facing components in many plasma experiments are initially graphitic in structure, at the nm length scales corresponding to these simulations. Note that the present analysis does not include the averaging over orientation of graphite planes that would be required for a rigorous comparison with polycrystalline materials such as ATJ graphite or carbon fiber composites. The evolution of the C and D density profiles is illustrated in Figure 2, at fluences up to $3.54 \times 10^{20}$ D m$^{-2}$.

The sharp peaks in the density profile indicate the layered graphite structure, at low fluences and well beneath the interface. Upon bombardment, however, the surfacemost layers lose their layered structure and become amorphous. At a fluence of $0.98 \times 10^{20}$ D m$^{-2}$ (red, solid curves in Figure 2. Density profiles of carbon (upper panel) and hydrogen (lower panel), in atom/Å³, for a graphite surface under bombardment by 20 eV D atoms as simulated with the REBO potential, for fluences as indicated in the legend in units of $10^{20}$ D m$^{-2}$. The $z$ coordinate is provided in units of Å, where the initial position of the interface at zero fluence is approximately $z = 24$ Å.
Fig. 2), the bombardment has only affected the structure of the two graphite layers closest to the interface. The outermost layer, originally near $z = 24 \AA$, has become largely amorphous, while the second layer has become somewhat disordered but preserves much of its planar structure. This is confirmed by the D density, which shows that D atoms are attached to the upper and lower surface of the second graphite layer (note the lack of D directly at the $z = 20 \AA$ position of the second layer itself), and are fully embedded throughout the now amorphous outer skin.

At higher fluences of $1.96 \times 10^{20}$ D m$^{-2}$ (green, dashed curves in Fig. 2), this degradation has continued. The second graphite layer has become subsumed into the amorphous outer skin, which has grown to a width of approximately 20 Å, swelling some 15 Å above the initial position of the interface.

By the time the fluence has reached $3.54 \times 10^{20}$ D m$^{-2}$ (blue, short dashes in Fig. 2), the third layer of graphite has begun to be modified, binding a substantial amount of hydrogen. The outer two layers have expanded considerably, growing to a width of approximately 50 Å, and reaching some 45 Å above the position of the initial interface. As it has swollen, the density of the modified surface has also dropped accordingly. Experimental studies have also observed the formation of low-density, amorphous regions under bombardment, although for tungsten rather than carbon surfaces.[26] The low-density region is highly fragmented, as is visible from the inset of Figure 2. When the system at a fluence of $3.54 \times 10^{20}$ D m$^{-2}$ is simulated, post-impact, for an additional 500 ps with no thermostat and no bombardment, only 40 of the approximately 440 atoms in the low-density region desorb from the surface, illustrating that most of the fragments are properly described as part of the surface. It is still possible, however, that this low-density region may be an artifact of the unrealistically small time between impacts, and that lower fluxes would allow for more complete annealing of the damaged surface; this question cannot be resolved from the current simulations.

These dramatic changes, and the difference in behavior when compared to the a-C:D system, are more clearly illustrated in Fig. 3, where we directly show the evolution of density as a function of fluence, for both the a-C:D and graphite initial substrates. In this figure, the surface is characterized by the C and D density in the modified surface layer (not the full system). To calculate this surface-only density of C and D, the boundaries of the modified surface were taken to be those $z$ planes at which the density began to differ substantially from the unmodified surface, for a-C:D, or at which the density drops to 10% of the peak density in the modified surface, for graphite.

The evolution of the a-C:D surface is illustrated for both of the independently constructed surfaces in Fig. 3 (blue [short dashed] and magenta [dotted] curves). Although these two

**Figure 3.** Evolution of the properties of the impact-modified surface, characterized by C and D density, as a function of fluence, under 20 eV D impacts. The surface evolution is shown for two distinct a-C:D surfaces modeled with the REBO potential, and graphite modeled with both REBO and AIREBO. Labels on each point indicate fluences, in units of $10^{20}$ D m$^{-2}$. 
simulations do not demonstrate identical evolution of surface properties, they are qualitatively quite similar. The difference between the two curves — on the order of 0.01 atom/Å³ at corresponding fluences — serves as an indication of the level of statistical error that can be expected from independent realizations of different surfaces with the same average properties. We also observe from these two surface evolution trajectories that the system has not reached a true steady state, as the C and D density continue to evolve slowly at fluences of ~1.0 × 10²⁰ D m⁻². The evolution of the surface has slowed, however, with the rate of change in the density being somewhat slower than at lower fluences. Previous simulations of a-C:D at 300 K have found that a steady state is reached at fluences of 1.0–2.0 × 10²⁰ D m⁻², with the sputtering yield and structural properties such as surface density becoming constant to within statistical fluctuations.[13; 17]

The bombardment of the graphite surface under REBO (red, solid curve in Fig. 3), on the other hand, shows behavior that is strikingly different from that of the a-C:D surfaces. The initial graphitic state is far from a-C:D in this density space, and the surface quickly evolves towards lower C density and higher D density, as expected. However, rather than approaching the same region in density space that the a-C:D system evolves towards, the graphite system never accumulates as much D, and eventually becomes much less populated with C atoms. And, surprisingly, the D density does not increase monotonically, but begins to decrease rapidly above fluences of 2 × 10²⁰ D m⁻² as the surface swells, as was already observed in Fig. 2.

The graphite system was also simulated with the AIREBO potential, in order to evaluate the effect that the potential has on the surface structure. The evolution of the modified surface of this system is also shown in Fig. 3 (green, dashed curve). Interestingly, the evolution of the AIREBO surface follows a very similar trajectory in density space to that of the REBO surface, although they are not identical. Generally, the C and D densities at a given fluence are identical to within the ~0.01 atom/Å³ tolerance that can be attributed to the statistical difference between different realizations. It would be very interesting to see whether the AIREBO potential also predicts the dramatic swelling and decrease in density exhibited with REBO at fluences above 2 × 10²⁰ D m⁻². Unfortunately, however, the added computational expense of the AIREBO potential meant that these higher fluences could not be reached as part of the current study.

Although the properties of the modified surface layers appear similar when characterized by just their C and D density, their structures are, in fact, different in other respects. This is illustrated in Fig. 4, which compares the density profiles for REBO and AIREBO bombardment of the graphite surfaces at comparable fluences of 1.6 × 10²⁰ D m⁻². Here it can be seen that, while the density of the modified surface layer is comparable for both potentials, the width of the modified surface layers is quite different. At this fluence, the REBO bombardment has amorphized the outermost layer of graphite, which has begun to crosslink with the disordered second layer, while the D atoms penetrate as deeply as the upper surface of the third graphite layer, spanning the outermost 23 Å of the surface. Under bombardment with the AIREBO potential, however, the outermost graphite layer has become largely amorphous, but the second layer is largely unmodified, and binds very few hydrogens. The hydrogens are restricted to the outermost 12 Å of the surface, within the amorphous skin. Thus, while the densities of the modified surface layers are similar, the depth of the surface modification under AIREBO is approximately half that obtained with the REBO potential. This is consistent with earlier studies, which have found that the presence of the repulsive Lennard-Jones interactions in the AIREBO potential results in larger scattering cross sections,[27] and that adding repulsive nonbonded interactions decreases crosslinking between graphite layers.[19]

4. Conclusion
In this work, we have examined the evolution of both graphite and hydrogenated amorphous carbon surfaces under bombardment by 20 eV D, using molecular dynamics simulation. These
simulations reinforce results obtained in previous work, while providing new information regarding the assumption that there is a unique steady state surface composition for any given bombardment conditions.

In all cases examined, bombardment of a carbon-based surface by deuterium leads to erosion of the carbon content and accumulation of deuterium. This is true even when the initial surface is consistent with amorphous carbon that has been fully saturated with hydrogen.[25] The detailed evolution of the surface composition is complex, however, and depends on the initial surface.

Independent simulations of amorphous carbon surfaces that are similar in their composition, but differ in atomic detail, result in very similar evolution of surface composition, as measured by density. An initially graphitic surface, on the other hand, evolves towards a composition that appears to be distinct from that approached by the a-C:D, and is considerably less dense. In addition, the evolution of the initially graphitic surface is complex, with non-monotonic changes in hydrogen density. This conclusion is significant, as it appears to suggest that the “steady state” surface that is generated by bombardment, and which has been shown to have large effects on the sputtering properties of a surface, is not only a property of the bombardment conditions, but retains some dependence on the starting state of the surface, at least at the fluences examined here. Because the surfaces were still evolving at the highest fluences considered here, we are unable to say definitively whether the two surfaces are in fact approaching different steady states. Extending this study to higher fluences in order to answer this question more conclusively will be important in comparing simulation to experiment. In addition, it will be important to analyze the sputter yield of these modified surfaces, in order to determine the effect of the modified surface structure on experimentally measurable properties such as sputter yield. In the meantime, this study reiterates the importance of matching the simulated bombardment conditions to the target experiment as closely as possible, not just in terms of the state of the impacting particle beam or plasma, but also in the starting substrate material.

The use of the more complete AIREBO potential, which treats nonbonded interactions that are ignored in the REBO potential, generated modifications to the graphite surface that are similar in composition to those produced with REBO, although the modification depth was less with the AIREBO potential, due to the larger cross section, and hence greater stopping power, that results from including noncovalent exchange repulsion. The similarity in structure obtained with the two potentials provides some justification for the widespread use of the computationally less expensive REBO potential, although it remains to be examined whether the sputtering properties are similar between the two potentials.
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