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Sputtering of amorphous hydrogenated carbon by hyperthermal ions as studied by tight-binding molecular dynamics

A.V. Krasheninnikov [a,*], K. Nordlund [a], E. Salonen [a], J. Keinonen [a], C.H. Wu [b]

[a] *Accelerator Laboratory, University of Helsinki, P.O. Box 43 (Pietari Kalmin Katu 2), FIN-00014 Helsinki, Finland*
[b] *EFDA, MPI für Plasmaphysik, D-85748 Garching bei München, Germany*

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Abstract

Although the mechanisms of the erosion of carbon-based materials by low-energy hydrogen ions have recently been addressed from an atomistic point of view [see e.g. Phys. Rev. B 63 (2001) 195415], it is not clear yet whether the quantum-mechanical effects are important for an adequate description of the erosion. We now study the low-energy erosion mechanisms by tight-binding molecular dynamics, which accounts for the quantum-mechanical nature of the interactions between the impinging particle and surface. We simulate the ion-assisted bond breaking in simple model systems like carbon dimers and also model sputtering from realistic hydrogenated carbon surfaces. Our simulations confirm the empirical potential results on the low-energy erosion mechanism, and help one to distinguish between the different mechanisms of the surface erosion.

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1. Introduction

One of the important applications of the energetic particle–surface interaction theory is the prediction of the erosion of tokamak fusion reactor walls. This erosion occurs due to impacts of low-energy hydrogen ions and neutrals escaping from the core plasma due to plasma instabilities [1]. During the fusion reactor operation, the plasma-facing divertors will continuously be bombarded with hyperthermal (1–100 eV) and high-flux (10^{19}–10^{20} ions/cm^2 s) hydrogen atoms and ions. This will result in two deleterious effects: bremsstrahlung-mediated cooling of the plasma by impurities eroded from the walls and the degradation of mechanical and thermal characteristics of the reactor walls.

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[*] Corresponding author. Tel.: +358-9-19150010; fax: +358-9-19150042.

E-mail address: akrashen@beam.helsinki.fi (A.V. Krasheninnikov).

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Carbon- and hydrogenated carbon-based materials are promising candidates for coating tokamak divertor plates because of their excellent plasma-facing properties, such as high cohesive energy and melting point. A drawback of such materials is the low carbon atomic number which gives rise to a relatively high sputtering yield as compared to that for high-Z materials such as tungsten and molybdenum [2]. Besides this, the sputtering of carbon by hydrogen ions and neutrals occurs at low energies of about 10 eV [3–5]. This phenomenon cannot be explained within the framework of the conventional theory [6] of physical sputtering due to the transfer of kinetic energy from the impinging particles to the target atoms. Thus, understanding the low-energy erosion mechanisms may not only suggest a way of decreasing the yield, but also reveal new physics of energetic particle–surface interactions.

Since sputtering is inherently an atomic-scale effect, atomistic computer simulations are well suited and widely used for studying it. Using molecular dynamics (MD), we recently demonstrated that the bombardment of amorphous hydrogenated carbon (a-C:H) surfaces with low-energy hydrogen ions can lead to erosion yields far exceeding those for collisional processes alone [7–9]. The underlying mechanism, which we call swift chemical sputtering, differs from standard collisional physical sputtering mechanisms in the sense that the sputtering stems from the direct breaking of chemical bonds rather than from the ballistic collision leading to a large momentum transfer.

In our simulations, we used an empirical potential (EP) [10] to describe the interactions between atoms in the target and between the impinging particle and the target atoms. However, although the EP approach has been demonstrated to work very well for graphite and diamond [10], it has proved to have some problems in describing technologically important amorphous carbon materials [11] where the angles between bonds strongly differ from those in graphite and diamond. The transferability problem may also be relevant to a-C:H into which any carbon system turns due to high-dose hydrogen irradiation in tokamak-type fusion devices [1]. Besides this, it is not quite clear to what extent quantum-mechanical effects are important in describing the bond breaking at low energies of impinging particles, so that a verification of the EP results [7–9] by more sophisticated methods is highly desirable to validate the swift chemical sputtering mechanism.

The goal of this paper is to model the erosion of amorphous carbon by impinging hydrogen atoms using quantum-mechanical methods and verify the EP results. We carry out tight-binding (TB) MD simulations, which in contrast to the EP models account for the quantum-mechanical nature of interactions in solids as well as of impinging particle–surface interaction. We also provide better comprehension of the underlying physics by considering, in addition to a-C:H, simple model systems. We also show how the experimentally observed hydrogen isotope effect [5] can be explained in terms of the swift chemical sputtering mechanism.

2. Method

We employed MD [12] to simulate the movement of atoms and ions in the system. The forces acting on the particles were calculated quantum mechanically for every time step within the framework of the TB approach [13]. We also carried out in this work EP simulations for juxtaposing our results with the already published data.

The main difference between the TB and EP methods is that the EP potential energy is described by an analytical function of atom coordinates usually fitted to experimental data, whereas in the TB method the energy is calculated by solving the Schrödinger equation for electrons in the field of atom cores, although the exact many-body Hamiltonian operator is replaced with a parametrized Hamiltonian matrix. The basis set usually is atomic-like so that it has the same symmetry properties as the atomic orbitals. We used a non-orthogonal self-charge consistent TB method [14,15] in which the parameters of the Hamiltonian were derived from ab initio calculations (a second-order expansion of the Kohn–Sham total energy in density-functional theory with respect to charge density fluctuations). Thus, no empirical parameter is present in the method and despite the approximations made this TB method retains the quantum-mechanical nature of bonding in materials, ensuring that the angular nature of the bonding is correctly described in far-from-equilibrium structures. Because of parameter fitting to the density function results, this method, unlike other TB schemes (where the parameters are chosen to describe equilibrium structures) describes the interaction of atoms at small interatomic separations, i.e., upon energetic collisions. The TB approach (with various parametrizations used) has been found to work well in modeling amorphous carbon–hydrogen systems [16–18] and the results (e.g., on partial correlation functions, bonding angles, etc.) are in agreement with those obtained by the first-principle methods [19].

The reason why we did not use first-principle (ab initio) methods [20] is a high computational cost of such methods. Since sputtering is a statistical process by its nature, modeling such processes demands carrying out a large number of simulation runs and collecting statistics. At the same time, a system must be about as large or larger than the characteristic region of ion-impact-induced perturbation (which is about 10 Å at the ion energies considered). All of these factors practically prevent the use of first-principle methods for such purposes. However, although first-principle methods generally provide the best overall accuracy, the TB approach is a reasonable compromise between the computational efficiency and the reliability of the model used.

3. Results

The swift chemical bond-breaking mechanism which governs the sputtering from amorphous hydrogenated carbon at low energies of incident hydrogen ions has been already addressed by the EP method [9]. When the impinging particle enters the space between two carbon atoms, the atoms are forced apart due to the repulsion between the carbon atom cores and the particle since at such short distances electrons do not shield the core–core repulsion.

To understand the mechanism in a more detailed manner, we consider a carbon dimer. This very simple model system makes it possible to distinguish between usual physical sputtering due to collisional, namely kinematic processes and swift chemical sputtering due to ion-assisted bond ruptures. This simple system also enables one to understand differences between the TB and EP models.

We consider a free carbon dimer and a moving hydrogen atom. Our goal is to break the C–C bond in the dimer by the impinging atom. If the H atom is moving along the axis passing through the C–C bond (a head-on collision, see Fig. 1), the transfer of the kinetic energy to the carbon atoms is maximal. If the energy of the H atom is low, the H atom will be just bounced back, see case (a), whereas the dimer will start moving as a single unit into the opposite direction after the impact (some energy is, of course, transferred to the dimer vibrational degrees of freedom). If the kinetic energy of the H atom is high, one of the carbon atoms will become energetic enough to break up the bond, see case (b). The minimum kinetic energy of the H ion (the threshold energy) for such a process is 37 eV for the EP model and 67 eV for the TB model. This difference originates from different values of the carbon dimer binding energy given by the TB and EP models. [1] Obviously, the bond breaking occurs at any energy of the impinging atom, which exceeds the threshold value. The bond-breaking event may be associated in this case with the physical sputtering in a macroscopic system (we assume here that the bond breaking always leads to sputtering, which is not entirely correct for surface bonds).

The other limiting case is the situation where the H atom is moving in the direction perpendicular to the C–C bond (the x-axis), see Fig. 2. For this geometry, three different events (and hence different final atom configurations) are possible.

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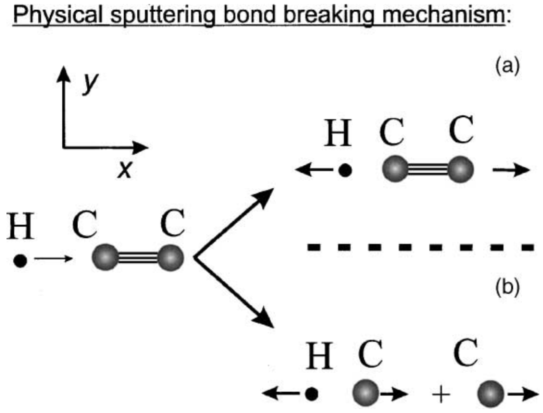
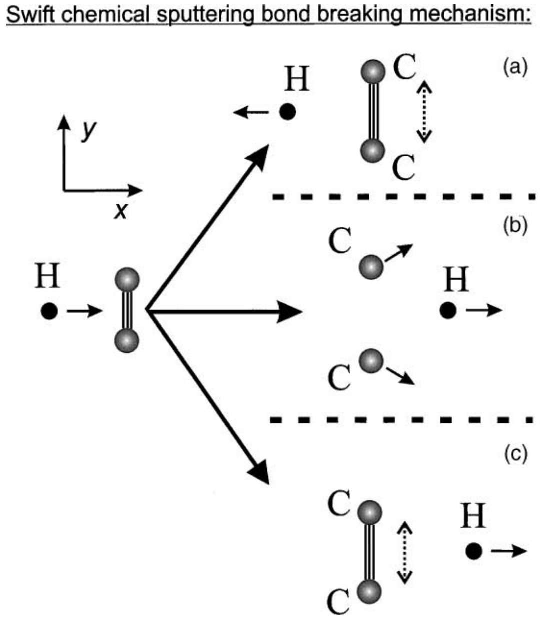
[1] The empirical potential model [10] gives for a carbon dimer a binding energy of 3.0 eV/atom, which is very close to the experimental value. The TB model [14,15] gives a larger value of 3.8 eV/atom (with the account of spin-polarization corrections). Overestimating the bonding energies for dimers is typical for TB models. However, the TB characteristics for bulk systems agree well with the experimental ones.



Physical sputtering bond breaking mechanism:

Fig. 1. Schematic representation of the physical sputtering process in a carbon dimer.



Swift chemical sputtering bond breaking mechanism:

Fig. 2. Schematic representation of the swift chemical bond breaking in a carbon dimer.

If the initial kinetic energy of the H atom is low, the H atom is reflected back, see Fig. 2(a). The impact also results in moving the dimer as a whole unit and in the excitation of the dimer vibrational degrees of freedom.

If the atom is energetic enough, then it will cause bond breaking in the dimer, case (b). However, the mechanism of bond breaking is quite different from that in the case of the head-on collision considered above. The bond rupture stems from the repulsion between the carbon and hydrogen atoms provided that they are close enough to each other. (As mentioned above, at low separations between the nuclei electrons do not shield the Coulomb repulsion of the cores.) The kinetic energy of the H atom is spent for bringing the H atom close enough to the C atoms. This is illustrated in Fig. 3, where the potential energy (actually, the total energy of the system, calculated within the framework of the TB model, minus the dimer energy) of the H atom is shown as a function of the x-coordinate of the H atom. The positions of the C atoms were kept fixed during the calculations of the energy. The origin is in the middle of the C–C bond.

The momentum p_y of the carbon atoms in the y-direction (or respectively their kinetic energy) is proportional to the effective force $\overline{f}_y$ acting on the carbon atoms and the effective time $\overline{\tau}$ when

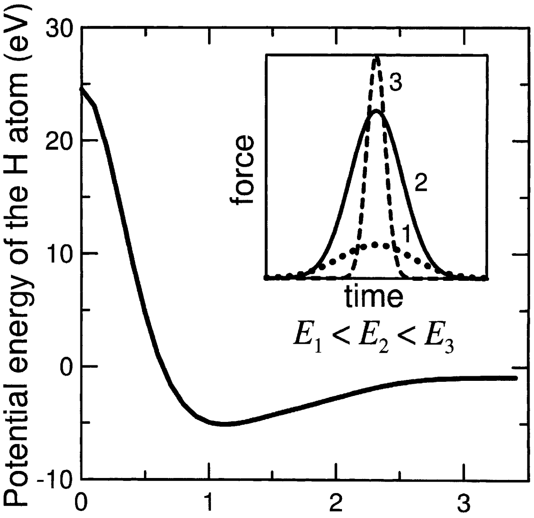


Fig. 3. Potential energy of the H atom as a function of the x-coordinate of the atom when it attacks the C–C bond. The positions of the C atoms were kept fixed during the energy calculations. The origin is in the middle of the C–C bond. The inset shows the schematic representation of the force acting on the carbon atoms vs. time for different initial energies of the H atom. The momentum of the carbon atoms in the y-direction is just the area below the curves.

the H atom is between the C atoms. More specifically,

$$p_y = \int_{-\infty}^{\infty} f_y(t, E_{\mathrm{kin}}[\mathrm{H}])\,\mathrm{d}t \approx \overline{f}_y \overline{\tau}, \tag{1}$$

where f_y is the force acting on the carbon atoms and $E_{\mathrm{kin}}[\mathrm{H}]$ the initial kinetic energy of the H atom. If $E_{\mathrm{kin}}[\mathrm{H}]$ is low, then the H atom returns back without entering the region between the C atoms, as a corollary of which $\overline{f}_y$ and the y momentum are small and the bond is not broken. This is schematically shown in the inset (dotted curve) in Fig. 3 where f_y is given as a function of time for different $E_{\mathrm{kin}}[\mathrm{H}]$. As follows from Eq. (1), p_y is the area below the curve. When the initial kinetic energy of the impinging particle is high enough for the H atom to stay for a long time in the region between the atoms (solid curve), the bond breaks. If we further increase the initial kinetic energy of the impinging particle, the bond breaking ceases, Fig. 2(c). The reason is that although $\overline{f}_y$ is large, the particle spends too little time in the region between the carbon atoms to cause any bond breaking ($\overline{\tau}$ is small). It is seen that there is an optimal energy for the bond breaking. The characteristic times of this process are very short, of the order of 10 fs.

Thus, the bond is ruptured in a certain range of particle energies, namely, between the two threshold energies of the bond breaking, $E_1 < E_{\mathrm{kin}} < E_2$. As follows from our simulations, the TB model gives $E_1 = 20.2$ eV and $E_2 = 24.2$ eV, whereas the corresponding EP result is $E_1 = 15.6$ eV and $E_2 = 48.2$ eV. The difference in the threshold energies originates from different binding energies of the carbon dimer as calculated within different approximations (see footnote 1).

The difference is not related to the effective cut-off radii of the models since for a dimer changing the cut-off alters the shape of the atom potential well, but not its depth. Note, however, that the value of the cut-off may have profound effect on the yield in many-atom systems, as discussed below.

For this orientation of the dimer and the impinging particle, the bond breaking may be associated with the swift chemical sputtering in bulk systems. We stress here once more that, unlike the first geometry considered above (Fig. 1), bond breaking occurs in a certain region of incident particle energies. For real multi-atom system and mixed geometries both mechanisms (physical and swift chemical bond breaking) can work simultaneously. However, as seen from the dimer simulations, the swift chemical sputtering occurs at energies of incident particles lower than those needed for physical sputtering. Thus, this mechanism governs the low-energy erosion.

Our simulations of bond-breaking events in a carbon dimer also enable us to explain qualitatively the isotope effect [5]. As experiments indicate, if we replace hydrogen with its isotopes (deuterium or tritium), we obtain higher sputtering yields from amorphous carbon for larger isotope masses although the energy of the impinging particles is the same.

We carried out simulations similar to those described above for the geometry when the deuterium or tritium atoms moves in the direction perpendicular to the dimer bond. We found that for deuterium the EP/TB threshold energies are $E_1 = 11.1/15.1$ eV, $E_2 = 77.6/45.0$ eV, whereas for tritium $E_1 = 9.0/13.6$ eV, $E_2 = 105.5/55.1$ eV (the first value is the EP result, the second one stands for the TB). It is seen that, the heavier the mass of the impinging particle, the larger the energy range where the bond breaking occurs. If the kinetic energy of the impinging particle is the same, then the higher its mass, the lower the speed. This means that, since the interaction potential is independent of the particle mass, heavy particles reside longer in the region between the carbon atoms than the light ones, giving rise to a larger momentum in the y-direction. Thus, the probability of bond breaking for tritium is the largest, and the bond-breaking probability for deuterium exceeds that for hydrogen. In experiments we have a continuous energy distribution of the impinging particles, and we can expect an increase in the bond breaking for heavy particles, and hence in the yield.

Having considered the bond breaking in the model system, we now proceed with the simulations of the carbon sputtering from a-C:H surfaces where many factors contribute to the sputtering. We dwell upon non-cumulative simulations (one impinging particle for every run). Our main goal here is to establish the correspondence between the sputtering yields obtained by the EP and TB calculations.

We developed and equilibrated 10 different simulation cells having roughly the size of a $10 \times 10 \times 10$ Å^3 cube and consisting of ≈ 200 atoms. The H/C ratio was 0.3–0.4, which roughly matched the experimental saturation value of bulk a-C:H [21,22]. The same cells were used for both the TB and EP simulations. Of course, energy minimization within the framework of these different models resulted in somewhat different atom positions.

The incident atoms were assigned a velocity towards the slab surface with a random off-normal angle between 0° and 20° and a random twist angle. The periodic boundary conditions were used in the x, y-direction (the z-axis was normal to the irradiated surface). The temperature of the cells was 300 K. Several hundred events were simulated for every cell and the results were averaged over all the cells. The criterion for a particle to be sputtered was that the distance between the slab surface and the particle is more than 4 Å but it still has a finite momentum. We used deuterium atoms as impinging particles. Other details of our simulation principles may be found in Refs. [7–9].

The carbon sputtering yield as a function of incident deuterium atom energy is shown in Fig. 4. Carbon atoms were usually sputtered as components of hydrocarbon C_nH_m ($n = 1, 2$; $m = 0, 1, 2, 3, 4$) species. The solid line (squares) stands for the yield calculated by the TB model, the dotted one (circles) corresponds to the EP simulations. It is evident from Fig. 4 that the TB simulations also give a finite carbon yield at low (<20 eV) energies. A thorough analysis of bond-breaking events indicated that it is the ion-assisted swift chemical sputtering mechanism which gives rise to bond breaking and carbon sputtering. At the same time, the yield is lower for the TB model than that for the EP model, which can be attributed to larger cut-off radii (i.e. larger interaction ranges as a result of which a sputtered carbon atom has higher probability of returning to the surface) and higher values of binding energies typical for the TB models. However, at higher energies the difference is small, within the statistical errors.

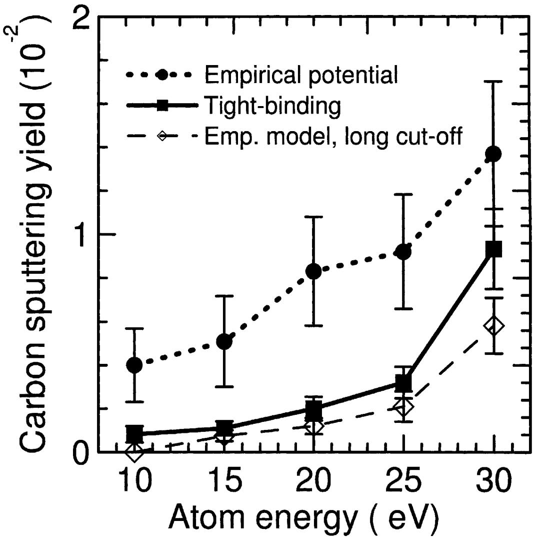


Fig. 4. Plot of the carbon sputtering yield as a function of incident deuterium energy.

In order to clarify the effects of increasing the cut-offs on the sputtering yield, we carried out similar EP simulations with a longer [23] cut-off of 2.46 Å (instead of 2.0 Å used in the original Brenner model). It is worth noting that longer cut-off radii are important for the adequate treatment of amorphous systems, e.g., for describing realistically the phase transitions in amorphous carbon systems [24]. The yield at the longer cut-off is also given in Fig. 4 (long-dashed line, diamonds). It is seen that the long cut-off results are very close to the TB results. Thus, the difference between the TB and the EP results with the original cut-off is likely due to different cut-off radii. Notice that both models give a finite yield at low energies of the impinging atom.

It should be noted here that the yield calculated in this work is less than that presented in our previous work [8]. This originates from the smaller simulation cells used in this work due to severe limitations on the system size related to computational expenses of the TB simulations. For such small systems (about 10 Å deep), the impinging particles have a lower probability to transfer all its kinetic energy to the slab (higher probability to pass through without any substantial interaction), as a corollary of which the yield proved to be lower. Besides this, slabs of smaller sizes have a larger fraction of surface atoms, which resulted in hydrogen outgassing from the slabs as a corollary of which the number of strong C–C bonds (usually in the sp^2 hybridization) was larger in the smaller simulation cells. However, we stress here that our goal was to compare the results of the TB and EP simulations but not to reproduce quantitatively the experimental situation.

Thus, since the TB quantum-mechanical simulations on sputtering from a-C:H systems give a finite yield at low energies of the impinging ions, they validate the results obtained within the framework of the EP models.

4. Discussion and conclusions

In this work, we carried out quantum-mechanical TB atomistic simulations of carbon sputtering from amorphous hydrogenated carbon. We also employed EP models in order to estimate how much our results depend on a particular model used. We simulated ion-assisted bond-breaking events (which can result in sputtering) for both carbon dimers—simple but physically transparent model systems—and realistic hydrogenated carbon slabs. Our calculations for the dimers illustrate the difference between the physical and swift chemical sputtering mechanisms and shed light on the elemental bond-breaking process. Our results make it also possible to explain qualitatively the isotope effect observed in experiments.

Although the two force models used in this study are quite different from a mathematical viewpoint, they both give finite sputtering yield at low energies of impinging particles. Thus, it can be stated that this work with a quantum-mechanical treatment of the atomic system validates the bond-breaking (and subsequently, erosion) mechanism, though the carbon sputtering yields given by the empirical and TB models differ quantitatively.

On the other hand, the scatter in experimental data [3,5,25,26] at this low ($\leqslant 30$ eV) hydrogen irradiation energies, due to different experimental methods and the use of molecular projectiles instead of single atoms, makes it difficult to determine which model really gives the most accurate quantitative results.

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