

## Tight-Binding Atomistic Simulations of Hydrocarbon Sputtering by Hyperthermal Ions in Tokamak Divertors

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### Abstract

Recent empirical potential simulations [5] explain from an atomistic point of view the mechanisms of the erosion of carbon-based fusion reactor walls by low-energy hydrogen ions coming from the plasma. However, it is not quite clear yet to what extent the quantum-mechanical effects are important for an adequate description of the erosion. Making use of tight-binding molecular dynamics, which accounts for the quantum-mechanical nature of impinging particle-surface interaction, we re-examine the low-energy erosion mechanisms by simulating the ion-assisted bond breaking in simple model systems like carbon dimers and by modeling sputtering from realistic hydrogenated carbon slabs. Our simulations confirm the empirical potential results on the low energy bond-breaking mechanism, and help one to differentiate between the different mechanisms of the erosion.

### 1 Introduction

Understanding the interaction of low-energy collisional plasmas with solid surfaces is essential for many applications. One of the most important is the development of first wall materials for thermonuclear fusion reactors. During the operation of such reactors, the plasma-facing materials are continuously bombarded with low-energy (1-100 eV) and high-flux ( $10^{19} - 10^{20}$  ions/cm<sup>2</sup>s) hydrogen atoms and ions, which results in two deleterious effects: bremsstrahlung-mediated cooling of the plasma by impurities etched from the walls and the degradation of mechanical and thermal characteristics of reactor walls. The latter effect limits the operational age of the materials to unacceptably short periods of time.

Carbon-based materials are widely used in tokamak divertors owing to their excellent plasma-facing properties. At the same time, the low atomic number of carbon gives rise to a relatively high sputtering yield as compared to that for "high-Z" materials, e.g., tungsten [1]. Moreover, experiments [2, 3, 4] indicate that the erosion of carbon by hydrogen ions and neutrals occurs at energies of about 10 eV, which is well below the threshold 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.

Inasmuch as the erosion is an inherently atomic-scale effect, atomistic computer simulations are excellent tools for studying it. Making use of empirical potential (EP) molecular dynamics, we recently demonstrated that low energy hydrogen bombard-

ment of carbon can lead to erosion yields far exceeding those for a collisional processes alone [5, 6, 7]. The underlying mechanism, which we call swift chemical sputtering, differs from standard collisional physical sputtering mechanisms in the sense that it is due to the direct breaking of chemical bonds and, hence, no ballistic collision leading to a large momentum transfer is required.

It should be noted, however, that although the EP approach has been demonstrated to work very well for graphite and diamond [8], it proved to have some problems in describing the technologically important amorphous carbon materials [9] where the angles between bonds strongly differ from those in graphite and diamond. The transferability problem may also be relevant to amorphous hydrogenated carbon (*a*-C:H) which any carbon system turns into due to high-dose hydrogen irradiation in tokamak-type reactors [10]. Thus, it is not quite clear to what extent quantum-mechanical effects are important at these low energies, so that a verification of the EP results [5, 6, 7] by more sophisticated methods is highly desirable to validate the swift chemical sputtering mechanism.

In this paper, we present the results of tight-binding molecular dynamics simulations (which, in contrast to EP models, account for the quantum-mechanical nature of interactions in solids as well as of impinging particle-surface interaction) of the erosion of amorphous carbon by impinging hydrogen atoms. Our goal here is to check the EP simulations and 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 [4] can be explained by swift chemical sputtering mechanism.

## 2 Method

We used molecular dynamics [11] to describe the movement of atoms and ions in the system by deriving the forces affecting the particles from either classical potential energy functions or from the total energy of the system calculated quantum-mechanically for every time moment (the adiabatic approach is usually used; thus electron and ion degrees of freedom are treated separately). This procedure was repeated in consecutive time steps.

As for the energy and force calculations, although first-principle (*ab initio*) methods [12] generally provide the best overall accuracy, the use of such methods is hindered by severe requirements on computational resources needed. We stress here that sputtering is a statistical process by its very nature. Hence, modeling such processes demands carrying out a large number of 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 at least 10 Å even at low ion energies). All of these practically prevent using first-principle methods for such purposes.

The tight-binding (TB) methods [13] lie between the very accurate but expensive first-principle methods and the fast but limited empirical methods. 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, although the exact many-body Hamiltonian operator is replaced with a parametrized Hamiltonian matrix. The basis set usually is atomic-like in that it has the same symmetry properties as the atomic orbitals. In the latest versions of the TB method [16], the parameters of the Hamiltonian are derived from *ab initio* calculations. Thus, no

empirical parameter is present in the method and, despite the approximations made, TB methods retain the quantum-mechanical nature of bonding in materials, ensuring that the angular nature of the bonding is correctly described in far-from-equilibrium structures. This approach has been found to be qualitatively correct for modeling amorphous carbon hydrogen systems [14, 15].

In this paper, we employ a non-orthogonal self-charge consistent (SCC) TB parameterization [16]. This formalism has been widely tested for simulating various systems [17]. It is based on a second-order expansion of the Kohn-Sham total energy in density-functional theory with respect to charge density fluctuations. If charge fluctuations are not important for particular problems, this method, as many other TB methods, makes it also possible to disregard the fluctuations, thus increasing substantially the computational efficiency. We used both SCC and non-SCC modifications in our simulations. In general, the majority of results was obtained within the framework of the non-SCC method, since our results proved to be qualitatively the same for both modifications.

### 3 Results

Before carrying out the atomistic simulations on low-energy sputtering from amorphous carbon, it is instructive to illustrate the swift chemical bond-breaking mechanism by the example of a carbon dimer. This is a very simple model system, which, however, makes it possible to distinguish between usual physical sputtering due to collisional, i.e., kinematic processes and swift chemical sputtering due to ion-assisted bond ruptures.

Our goal here is to break the C-C bond in the dimer by an impinging hydrogen 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 carbon atoms is maximal. In that case, if the energy of the H atom is low, the H atom is just bounced back, see case (a), whereas the dimer starts 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). However, if the kinetic energy of the H atom is high, one of the carbon atoms becomes 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 [18]. 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 bulk systems (it is suggested here that the bond breaking always leads to sputtering).

Now let us consider the situation when the H atom is moving in the direction perpendicular to the C-C bond (the  $x$ -axis), see the right-hand panel in Fig. 1. For this geometry, the outcome of the impact is more multifarious than that in the previous case. Three atom final configurations are possible. If the initial kinetic energy of the H atom is low, the H atom is reflected back, Fig. 1(c).

If the kinetic energy is high enough, then the atom causes the bond breaking in the dimer, case (d). However, the physics of bond-breaking is quite different from that in the previous case. The bond rupture stems from the repulsion between the carbon and hydrogen atoms provided that they are close enough to each other (at low separations between nuclei electrons do not shield the Coulomb repulsion of the cores).

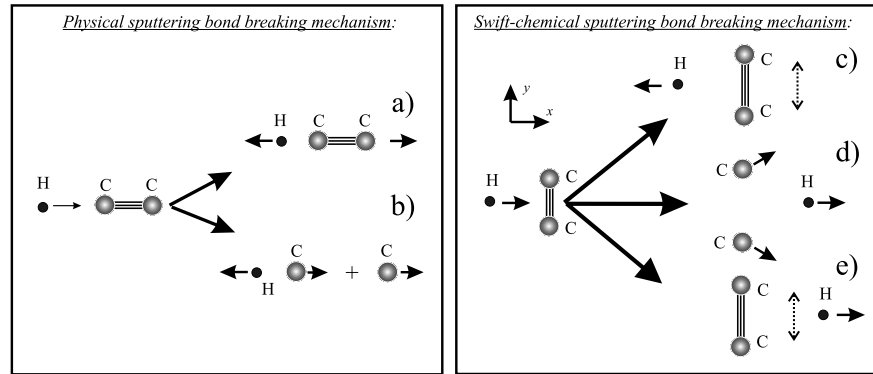


Fig. 1: Schematic representation of the bond breaking process by the example of a carbon dimer. The processes depicted in the left-hand panel may be associated with the physical sputtering in a bulk system, and those in the the right-hand panel with the swift chemical sputtering. See text for details.

The kinetic energy of the H atom is spent for moving the H atom close enough to the C atoms. The momentum of the carbon atoms in the  $y$ -direction (or, respectively, the kinetic energy) is proportional to the characteristic time during which the H atom is between the C atoms. If the kinetic energy is low, then the H atom goes quickly back, as a corollary of which the  $y$ -momentum is small and the bond is not broken. When the initial kinetic energy of the impinging particle is high enough for the H atom to stay long enough in the region between the atoms, the bond breaks. We stress here that the characteristic times are still very short, of the order of 10 fs.

However, if the initial kinetic energy is very high, the particle goes too quickly to cause bond breaking. Thus, the bond is ruptured at energies between the upper and lower bounds (threshold energies on the bond breaking,  $E_1 < E_{kin} < E_2$ . As follows from our simulations, the TB model gives  $E_1 = 20.2$  eV;  $E_2 = 24.2$  eV, whereas the corresponding EP model result is  $E_1 = 15.6$  eV;  $E_2 = 48.2$  eV. The difference in the values originates from different binding energies of the carbon dimer as calculated within different approximations, but it is not related to the effective cutoff radii of the models. Note, however, that the value of a cutoff may have profound effect on the yield in many-atom systems. For this geometry of the colliding particles, the bond breaking may be associated with the swift chemical sputtering in bulk systems. We stress once more that, unlike the first geometry considered above, bond breaking occurs in a certain region of incident particle energies. For real multi-atom system and mixed geometries both mechanisms 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.

Simulations of the bond-breaking in a carbon dimer by energetic particles also enables one to explain qualitatively the isotope effect [4]. It has been experimentally observed that irradiation of carbon with low-energy hydrogen isotopes gives rise to higher sputtering yields with increasing isotope mass.

Using deuterium and tritium atoms as impinging particles, we carried out the simulations similar to described above for the geometry when the particle moves in the direction perpendicular to the dimer bond. We found that for deuterium 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 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 is, the lower the speed. This means that, since the interaction potential is independent of the particle mass, heavy particles spend more time in the region between the carbon atoms than the lighter ones, giving rise to a larger momentum in the  $y$ -direction. Thus, the sputtering yield for tritium is the largest, whereas the yield for deuterium exceeds that for hydrogen. Since in experiments we have a continuous energy distribution of the impinging particles, for heavy particles we will have an increase in bond breaking, and, hence, in the yield.

Now we proceed with the non-cumulative simulations (one impinging particle for every run) on sputtering from  $a$ -C:H surfaces. Our main goal here is to establish the correspondence between the sputtering yields obtained by the EP and TB calculations.

Analogously to Ref. [5, 6, 7], we developed and equilibrated 10 different simulation cells having roughly the size of a  $10 \times 10 \times 10 - \text{\AA}^3$  cube and consisting of  $\approx 200$  atoms. The H/C ratio was 0.4, which matched the experimental saturation value of bulk  $a$ -C:H [20, 21]. The incident atoms were assigned a velocity towards the slab surface with a random off-normal angle between  $0^\circ$  and  $20^\circ$  and a random twist angle. The temperature of the cells was 300 K. Several hundred events were simulated for every cell and the results were averaged over all cells. The criterion for a particle to be sputtered was that the distance between the slab surface and particle is more than  $4 \text{\AA}$  but it still has a finite momentum. We used deuterium atoms as impinging particles. Other details of our simulation may be found in [5, 6, 7].

In Fig. 2 we present a plot of the carbon sputtering yield as a function of incident deuterium atom energy. Carbon atoms were usually sputtered as components of hydrocarbon  $C_nH_m$ ,  $n = 1, 2$ ,  $m = 0, 4$  species [19]. The solid line stands for the yield calculated by the EP model, the dashed one corresponds to the TB simulations. As follows from Fig. 2, the TB simulations also give a finite carbon yield at low ( $< 20$  eV) energies. A thorough analysis of bond breaking events evidences 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, which can be attributed to larger cutoff 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 error bars.

It should be noted here that the yield calculated by the EP model in this work is less than that presented in our previous work [5]. This originates from the smaller simulation cells used in this work due to severe limitations on the system size related

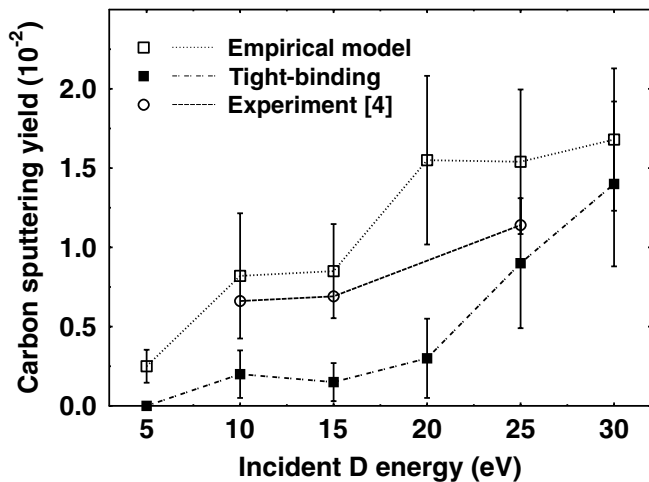


Fig. 2: Plot of the carbon sputtering yield as a function of incident deuterium atom energy.

to computational expenses of the TB simulations. For such small systems (about 10 Å deep), the impinging particles have 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. However, we stress here that our goal was to compare the results of the TB and EP simulations. Besides this, our theoretical results are in line with experimental ones [4], which are also presented in Fig. 2.

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

We carried out quantum-mechanical tight-binding atomistic simulations of carbon sputtering from amorphous hydrogenated carbon which covers the carbon divertor plates in tokamak fusion devices. We modeled ion-assisted bond-breaking events (which can result in sputtering) for both simple model systems like carbon dimers and realistic hydrogenated carbon slabs. Our simulations on the the carbon dimers illustrate the difference between physical and swift chemical sputtering mechanisms and sheds light on the elemental bond-breaking process. Our results make it also possible to explain qualitatively the isotope effect observed in experiments.

The two force models used in this study, the TB and empirical, have practically nothing in common. However, the simulations with the former method, which gives a quantum-mechanical treatment of the atomic system, still produce the same C–C bond-breaking mechanism observed with the empirical potential energy function. Thus, it can be stated that our present work validates the bond-breaking (and subsequently, erosion) mechanism.

The carbon sputtering yields given by the empirical and tight-binding model simulations differ quantitatively, especially at low energies. On the other hand, the lack of experimental data at this low (under 30 eV) hydrogen irradiation energies makes it difficult to determine which model really gives more accurate results. Also, it is known that even experimental carbon sputtering yields can differ significantly from each other [4, 22, 23]. Factors contributing to this are the different experimental methods used, and the use of molecular projectiles instead of single atoms.

Finally, we note that while the present study validates our previous results on one form of chemical sputtering, it is clear that more detailed experiments and theoretical work on the low energy sputtering is required before a comprehensive and clear picture of the chemical sputtering of carbon is obtained.

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