

# Bond-breaking mechanism of sputtering

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**Abstract.** – Energetic ions are known to be able to erode atoms from a solid even when a collisional mechanism can not transfer enough kinetic energy from the impinging ions to substrate atoms to overcome the surface binding energy. We now describe how low-energy ions can cause erosion of atoms and molecules by colliding with and breaking chemical bonds between the atoms. In the particular case of hydrogen bombardment of amorphous carbon networks, we further show that this can lead to erosion yields far exceeding those expected for a collisional process alone.

*Introduction.* – The erosion of atoms from a solid surface by energetic ion bombardment is well understood when the kinetic energy of the impinging ions is sufficiently high to give a recoil energy to surface atoms large enough to directly kick them out from the surface. This process is called physical sputtering, and requires a transfer of kinetic energy of the order of  $\sim 10$  eV to substrate atoms [1]. Several experiments, however, have found erosion conditions where the transfer of kinetic energy by elastic collisions to substrate atoms is far too small to lead to appreciable physical sputtering yields, but where the impinging ion energy is also too large for description of the process as a conventional etching-type chemical reaction. A particularly important and timely example is the erosion of carbon-based fusion reactor wall materials. In these materials, the erosion of carbon atoms and small molecules by  $\sim 10$  eV hydrogen ions is known to occur at yields orders of magnitude higher than expected by physical sputtering [2,3]. This poses a serious problem for maintaining a stable fusion plasma, as well as obtaining a reasonable lifetime for the plasma-facing materials.

The low-energy erosion regime is frequently assumed to be due to some sort of bond-breaking mechanism, and hence often called (ion-assisted) chemical sputtering, but a true understanding of how the erosion actually occurs is missing [3–5]. While there has been detailed quantum mechanical [6] and molecular dynamics (MD) studies [7,8] of low-energy etching of silicon by F and Cl ions, the observed mechanisms, such as  $S_N2^{(1)}$ , have been

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<sup>(1)</sup>Nucleophilic substitution

chemical (preferential bonding of surface atoms to the impinging ions), and thus should not have a strong dependence on the ion isotope. Experimental studies of carbon bombardment by  $\sim 10$  eV H and D ions by Mech *et al.* [9], however, do show a significant isotope effect.

We now use a molecular dynamics simulation model, capable of both describing chemical bonding, high-energy recoiling atoms, and bond breaking [10, 11], to study bond-breaking erosion mechanisms by low-energy hydrogen ions.

*Method.* – The atomic-scale interactions of hydrogen ions<sup>(2)</sup> impinging on amorphous hydrogenated carbon (*a*-C:H) surfaces were studied with classical MD simulations. Because of the large number of atoms needed, no other computer simulation method is better suited for this task. We chose to study this system because on one hand a good interatomic force model is available, and on the other hand there is much experimental data available on it, since it is a material with good resistance to radiation damage [12]. As the force model we used the empirical Brenner-Beardmore many-body potential energy function, which is a modified version of the original Brenner hydrocarbon potential [10, 13]. The potential was originally fitted to describe solid carbon structures and hydrocarbon molecules, and has been successfully used for various hydrocarbon simulations [13–15]. We used the parameter set II, since it gives a more accurate carbon-carbon bond stretching constants, and a later modified parametrization [16].

Simulation cells consisting of 500 atoms were prepared with a H/C ratio of 0.4, matching the experimental saturation value of bulk *a*-C:H [17, 18]. The cells were equilibrated for various temperatures, and atoms within a distance of 2 Å from the bottom of the cell were fixed in order to simulate *a*-C:H bulk material instead of a thin film. Although this fixing is unrealistic *per se*, there are no large cascades in low energy bombardment such as that in the present work, whence very strong interactions never reach the fixed atoms. Periodic boundary conditions were applied in the *x* and *y* directions lying perpendicular to the surface normal *z*.

The incident ion (H or T) energy was either selected randomly from the Maxwell-Boltzmann energy distribution for a root mean square (rms) energy of 10 eV, or kept constant for each incident ion. The incident ion was assigned a velocity towards an *a*-C:H or *a*-C:T surface with a random off-normal angle between 0° and 20°, and a random twist angle. We ensured that the ion would not impact on the surface too close to the borders for two reasons: (1) the simulation cell temperature was scaled to a temperature between 300 and 1100 K within 2 Å from the borders using the temperature scaling method by Berendsen *et al.* [19], in order to keep the substrate temperature constant and to embed the energy brought into the cell by the impinging ion, and (2) an impact on the surface too close to the cell borders could create unwanted artificial effects across the borders. The cell was shifted a random distance in the *x*- and *y*-directions for each incident ion so that the whole surface could be used as a target for the bombardment. The impact cascades were followed for 2 – 3 picoseconds until the cell surface had cooled down, after which an ion was shot at the same original surface. Thus, our simulations were non-cumulative and concentrated only on *single* events. For each substrate cell at a certain temperature we ran a simulation of 2000 – 5000 incident ions, and for each run we observed  $\sim 10$  – 100 sputtered carbon atoms, either as monomers or in  $C_xH_y$  molecules. The impacts leading to carbon erosion were later studied in more detail.

*Results.* – The main carbon erosion mechanism in our simulations was the breaking of a carbon-carbon bond by the impinging hydrogen ion (fig. 1). Since hydrogen atoms only form a single bond, it is the carbon-carbon bonds that bind the surface carbon atoms to the bulk

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<sup>(2)</sup>The classical MD simulations can not take account of the charge state of atoms. Here we use the term ion to denote the incoming atom, regardless of its charge state.

carbon network. The  $\text{CH}_x$  erosion mechanism observed in our simulations is as follows. A low-energy incident ion enters the space between the carbon atoms (i.e. the covalent bond). The carbon atoms are forced apart from each other by a strong repulsion that is caused by the repulsive part of the (hydrogen-carbon) potential energy function. The minimum distance between the impinging ion and the carbon atoms is typically roughly  $0.7 \text{ \AA}$ , i.e. half the equilibrium C-C bond length.

To estimate the energetics of this process, we first note that *ab initio* calculations have shown that even a relaxed bond-centered hydrogen configuration in diamond has an energy of about 5 eV above the perfect lattice configuration [20, 21], which is quite enough to break a carbon-carbon bond. Fig. 1 shows that the carbon-carbon potential energy is increased by about 4 eV, which compares well with the results of the *ab initio* calculations, especially considering that the hydrogen ion never enters the exact midpoint of the C-C bond. The increase in the potential energy, which is clearly more than the bond strength of  $\sim 2 \text{ eV}$  per atom of typical  $sp^2$  and  $sp^3$  bonds, makes the bond breaking possible.

Since the impinging energetic ion forces the two carbon atoms apart very quickly, the surface carbon network does not have time to adjust itself to the new configuration. The separation, and consequently C-C bond breaking, can be further enhanced by the possible impact of the incident ion with one or several of the surface carbon network atoms. Finally, carbon atoms that are no longer bound to the bulk leave the surface along with any hydrogen atoms bonded to them. Erosion of  $\text{C}_2\text{H}_x$ , or larger hydrocarbon molecules, took place in a very similar way, caused by the bond-breaking mechanism described above. This time, however, the incident ion either broke a C-C bond deeper below the surface and the dangling hydrocarbon chain above the broken bond left the surface, or the ion was capable of breaking several C-C bonds of the surface atoms. The eroded atoms typically had kinetic energies of  $\sim 0.1 \text{ eV}$ .

At a substrate temperature of 300 K,  $\text{C}_2\text{H}_x$  molecules were the most common eroded hydrocarbons with a relative yield of 65% of all the sputtered molecules. The second most common type of molecule were methane-like molecules  $\text{CH}_x$  with a relative sputtering yield of about 35%. Only one solitary C atom was seen sputtering from one of the substrate surfaces. At 900 K, the relative yields were 11% for  $\text{CH}_x$ , 75% for  $\text{C}_2\text{H}_x$ , and 8% for  $\text{C}_3\text{H}_x$ . Four large  $\text{C}_5\text{H}_x$  molecules were also observed to leave the surfaces at this temperature, of which two fractured very soon to  $\text{C}_2\text{H}_x$  and  $\text{C}_3\text{H}_x$  molecules.

Our simulations with different cells at various temperatures showed that the difference in surface structure can lead to considerable differences in carbon yield. Simulation cells with an increased fraction of  $sp^2$  hybridized carbon atoms and a decreased fraction of  $sp^3$  hybridized carbon atoms at the surface led to higher carbon erosion yields<sup>(3)</sup>. A more detailed analysis revealed that the crucial factor is how many C-C bonds a carbon atom has. Carbon atoms with one or two C-C bonds are eroded more easily by low-energy ions than those with three or four. An ion with a fairly small energy can only break a C-C bond during the time between the first few collisions. Kinetic energy is transferred from the incident ion to the substrate atoms in elastic collisions and the maximum transferable energy is proportional to the kinematic factor  $T_{12} = 4M_1M_2/(M_1 + M_2)^2$  [22], where the masses of the two colliding particles are designated by  $M_1$  and  $M_2$ . A tritium ion with a kinetic energy of 10 eV can lose up to 6.4 eV of its kinetic energy in the first collision with a carbon atom and the possibility of C-C bond breaking in the following collisions is greatly reduced. Thus, erosion of carbon atoms with more than two bonds is highly unlikely.

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<sup>(3)</sup>For simplicity in the discussion, we use the notation  $sp^2$  and  $sp^3$  for all threefold- and fourfold-coordinated carbon atoms, respectively, regardless of whether the bond configuration corresponds exactly to the ideal hybridization geometry.

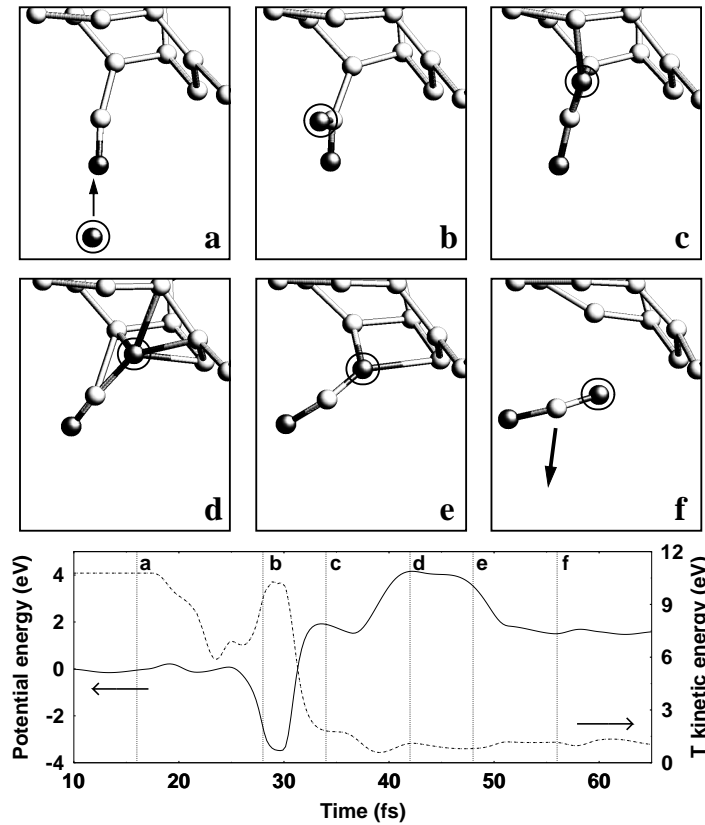


Fig. 1 – Illustration of the main carbon sputtering mechanism observed in our simulations. The initial movement direction of the impinging tritium (circled) is designated by the arrow. The light spheres represent carbon atoms and the darker ones T atoms. In the first snapshot (a) we see the original carbon configuration at the surface. The T ion slightly interacts with the outer carbon atom (b) and enters the space between the two carbon atoms (c). After colliding with the inner carbon atom the incident ion is reflected (d). The two carbon atoms are forced apart by the tritium ion between them. The C-C bond is broken (e) and the carbon atom leaves the sample with the two tritium atoms bonded to it (f). Some less important atoms from the simulation cell have been omitted in these pictures in order to show the mechanism more clearly. The graph below the snapshots shows the total potential energy of the two carbon atoms whose bond is broken, and the kinetic energy of the impinging tritium ion. The total potential energy at the start of the simulation has been chosen as the zero potential energy. The dashed lines show at what time the snapshots (a) - (f) have been chosen. At point (b) the potential energy of the two carbon atoms is lowered (and the T ion accelerated) when the ion forms a temporary energetically favoured state. Since the ion still has kinetic energy left, it leaves this state, and enters the energetically unfavourable, almost bond-centered state in (c) and (d), which then leads to bond breaking.

Figure 2 shows the typical temperature dependence for carbon erosion in our simulations. A clear maximum between 800 and 900 K can be seen. The increase in the yield in the temperature range 300 – 900 K is caused by the increase of the  $sp^2$  bonded carbon fraction at the surface during the slow ( $\sim 10 - 100$  ps) cell heating to the temperature in question, thus decreasing the total C-C coordination. Although the fraction of  $sp^2$  bonded carbon

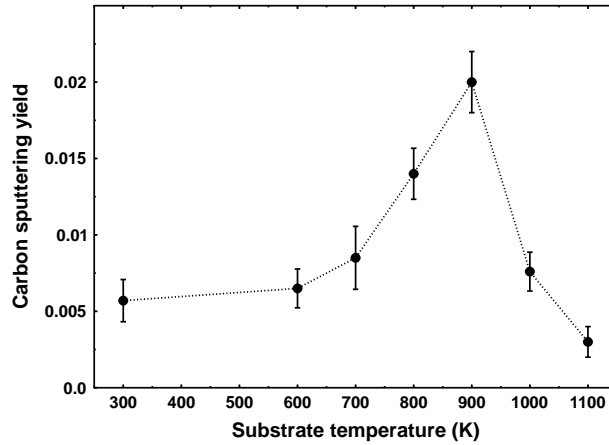


Fig. 2 – Carbon sputtering yield as a function of temperature in non-cumulative T bombardment simulations for one substrate simulation cell. Simulations using various substrate  $a$ -C:H or  $a$ -C:T cells showed a clear maximum for each of the cells at temperatures between 800 and 900 K, which compares well with experimentally observed maxima at  $\sim 600 - 900$  K [3, 9, 27].

increases with increasing temperature, a competitive process emerges at higher temperatures. We observed that the depth distribution of the sputtered species shifts towards the surface above 900 K. This indicates that at these temperatures the probability of bulk carbon bonding with hydrocarbon molecules, whose C-C bonds have been broken by the ion, is increased. This temperature effect was present in all the simulation cells, manufactured independently of each other. A more detailed analysis of the structural effects at different temperatures on the carbon erosion yield will be found elsewhere<sup>(4)</sup>.

Another factor strongly contributing to the carbon sputtering yield from  $a$ -C:H is the hydrogen content in the substrate, especially at the surface. In all of our substrate cells, at all temperatures, the H/C ratio was approximately 0.4. Our recent molecular dynamics calculations have, however, revealed that the carbon sputtering yield strongly depends on the hydrogen content at the surface [23]. Continuous bombardment of an  $a$ -C:H surface by low energy ( $\sim 1$  eV) hydrogen ions results in a surface with a supersaturated H/C ratio far exceeding the bulk saturation value of 0.4. This hydrogen shielding very efficiently decreases the H – carbon-carbon bond collision probability<sup>(5)</sup>, and consequently, the carbon sputtering yield roughly by an order of magnitude.

The energy dependence of the sputtering yield at a substrate temperature of 300 K was studied with simulations using the same kinetic energy for each incident ion. Breaking carbon-carbon bonds in order to remove even a single carbon atom from the surface carbon network, however, requires approximately an energy of 2 – 8 eV, depending on the bonding configuration. Removing larger hydrocarbon molecules requires naturally much more energy and one also has to take into consideration collisions with atoms not taking part in the bond breaking, that extract even more energy from the impinging particle. In physical sputtering, by contrast, the kinetic energy of the impinging ion is transferred to the surface atoms, proportional to the

<sup>(4)</sup>Work in preparation

<sup>(5)</sup>Although the physical meaning of the concept "an ion colliding with a chemical bond" may be hard to define precisely, we use it here simply as an easy-to-visualize description of the process of an energetic ion entering the space between two bonded atoms.

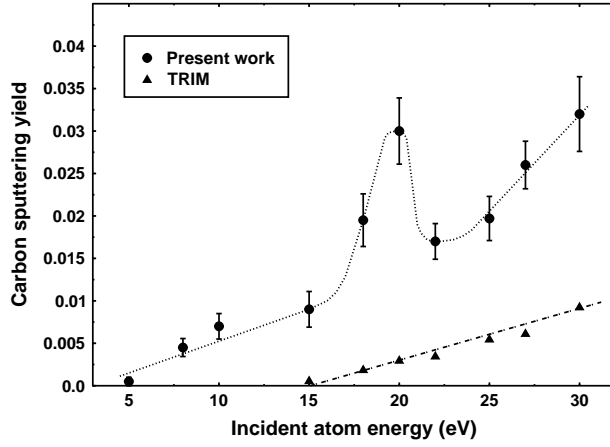


Fig. 3 – Carbon sputtering yield as a function of incident ion energy in our constant energy simulations of T impinging on *a*-C:T, overlaid on TRIM simulations of physical sputtering. The substrate temperature was 300 K for all the simulation runs.

kinematic factor  $T_{12}$ , in order to “kick them out” from the surface. The physical sputtering yield can be estimated with the TRIM program, which only considers binary ion-atom collisions [24, 25]. A comparison between our sputtering yields and those predicted by the TRIM code is shown in figure 3. The figure shows that yields of the order of magnitude observed in our simulations can not possibly be explained by physical sputtering alone. Also, a clear ion isotope effect on the sputtering yield could be seen in our modeling, whence the mechanism cannot be considered purely chemical either.

We observed a small local maximum for carbon yield corresponding to the ion kinetic energy of 20 eV (fig. 3). This indicates that at energies close to 20 eV, the bond-breaking mechanism has the highest probability, since the incident ions are energetic enough to break multiple bonds. At lower energies the yield is smaller since the bond breaking probability decreases. By running single impact simulations leading to carbon sputtering with same impact parameters and gradually lowering the incident ion energy, carbon sputtering was eventually suppressed. At higher energies, on the other hand, the ions penetrate too deep below the surface to cause sputtering, but the decrease in the chemical sputtering is gradually compensated by physical sputtering.

*Discussion.* – It is interesting to note that there is much experimental evidence on the temperature dependence of carbon erosion, ranging from thermal desorption [26] (i.e. pure chemical erosion) to high-energy ( $\sim 1.0$  keV)  $H^+$  ion bombardment [27]. Our modeling indicates that at least at intermediate (5 – 30 eV) energies the temperature dependence originates from a difference in the surface structure of the substrate at different temperatures. The maximum in our erosion yield occurs at about 800 - 900 K, which lies in the range of 600 - 900 K where the maximum is observed experimentally as well [3, 9, 27]. This has further implications for the use of *a*-C:H as a divertor material in tokamak fusion devices, where the ion energies correspond to the ones used in the present work.

We also observed the bond-breaking mechanism leading to erosion of both carbon and silicon from pure amorphous carbon and amorphous hydrogen-carbon-silicon mixtures, and thus believe the mechanism may be significant during light ion bombardment of any material

where atoms or molecules are bonded to a substrate by only a few covalent bonds. Several physical vapor deposition methods are based on bombardment of surfaces by ions with energies similar to those employed here [28]. Hence the realization that sputtering can be dramatically enhanced by bond breaking may be important in the modeling and development of such methods. Previous studies of low-energy etching [7, 8] describe the bond breaking as preferential bonding of ions to the surface atoms, leading to bond rupture. As well as an isotopic effect, the difference between these etching mechanisms and the mechanism we observed, is that the ion did not always bond to the sputtered molecules, but often merely broke the bond binding the carbon atoms to the surface.

In conclusion, we have described in detail how low-energy ions colliding with chemical bonds can lead to a bond-breaking sputtering mechanism, with sputtering yields far exceeding those expected for conventional physical sputtering.

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