

Swift chemical sputtering of covalently bonded materials*

K. Nordlund^{1,‡}, E. Salonen², A. V. Krasheninnikov¹, and J. Keinonen¹

¹Accelerator Laboratory, University of Helsinki, P.O. Box 43, FIN-00014 Helsinki, Finland; ²Laboratory of Physics and Helsinki Institute of Physics, P.O. Box 1100, FIN-02015 HUT, Helsinki, Finland

Abstract: Numerous experiments have shown that low-energy H ions and neutrals can erode amorphous carbon at ion energies of 1–10 eV, where physical sputtering is impossible, but at erosion rates which are clearly higher than those caused by thermal ions. In this paper, we will first review our computer simulation work providing an atom-level mechanism for how this erosion occurs, and then present some new results for H and He bombardment of tungsten carbide and amorphous hydrogenated silicon (a-Si:H), which indicate the mechanism can be of importance in a wide range of covalently bonded materials. We also discuss how the presented mechanism relates to previously described abstraction and etching mechanisms.

Keywords: sputtering; erosion; bond breaking; plasma-surface interactions; covalently bonded materials.

INTRODUCTION

The bombardment of carbon-based materials by low-energy (1–100 eV) H isotopes (H, D, or T) is of great interest in nuclear fusion reactors, since carbon composites are the material of choice for the reactor first wall or at least their parts which are subject to the highest heat loads, and there will be carbon redeposition on the first wall when a reactor is in use. Experiments have shown that this part, the divertor, is eroded by the incoming H due to sputtering of hydrocarbon molecules. The mechanism behind this effect was long unclear [1,2] since at the lowest energies (1–10 eV) physical sputtering of the wall is impossible.

At high temperatures, it is known that H atoms can enter the amorphous hydrogenated carbon (a-C:H) samples and change locally the bonding structure, resulting in the formation of a weakly bound molecule which can migrate to the surface and desorb [3]. But this requires thermal activation, and it cannot explain the observations of desorption between liquid nitrogen and room temperature with no temperature dependence [4].

Using molecular dynamics (MD) simulations of the bombardment process, we have described a new kind of chemical sputtering mechanism which can lead to instantaneous erosion of hydrocarbon species from surfaces [57]. The nature of the mechanism is easiest to understand by considering the model system of one H atom colliding with a C–C dimer. The most symmetric case possible is the one where the H atom moves perpendicular to the chemical bond toward the middle of it, see Fig. 1.

*Paper presented at the 17th International Symposium on Plasma Chemistry (ISPC 17), Toronto, Ontario, Canada, 7–12 August 2005. Other presentations are published in this issue, pp. 1093–1298.

‡Corresponding author

The momentum transfer in the y direction can be written

$$p_y = \int_{-\infty}^{\infty} f_y(t, E_{\text{kin}}^{\text{H}}) dt \approx \bar{f}_y \bar{\tau} \quad (1)$$

where f_y is the force acting on the carbon atoms and $E_{\text{kin}}^{\text{H}}$ the initial kinetic energy of the H atom. For the sake of the current argument, we simplify the integral to be a product $\bar{f}_y \bar{\tau}$, where \bar{f}_y is an effective average force during the collision, and $\bar{\tau}$ is an effective average time the H atom spends in the area of the C–C bond.

If the kinetic energy of the H ion $E_{\text{kin}}^{\text{H}}$ is low, the H atom returns back without entering the region between the C atoms. Then \bar{f}_y and the y momentum are 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 for a (relatively) long time $\bar{\tau}$ in the region between the atoms (solid curve), the bond breaks (Fig. 1b). If we further increase the initial kinetic energy of the impinging particle, the bond breaking ceases, Fig. 1c. The reason is that although \bar{f}_y is large, the particle spends too little time in the region between the carbon atoms to cause any bond breaking ($\bar{\tau}$ is short). Thus, there is a finite energy window in which the bond breaking can occur. The characteristic time of this process is very short, of the order of 10 fs. Because the mechanism involves atom bonding, requires kinetic energy, and is rapid, we have named it “swift chemical sputtering” (SCS) [8].

Swift chemical sputtering bond breaking mechanism:

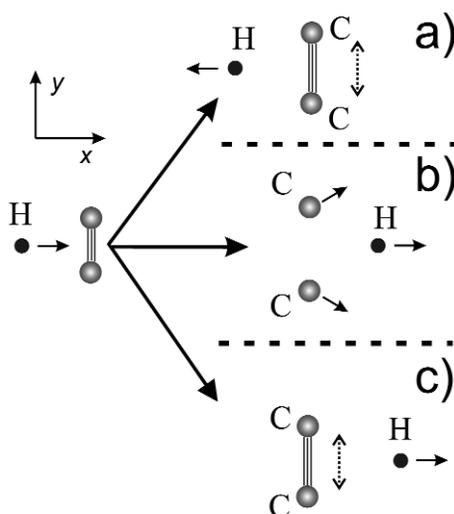


Fig. 1 Schematic representation of the swift chemical bond breaking in a carbon dimer. From ref. [7].

To rule out dependence on the choice of potential, we have shown that the effect occurs as described above using three varieties of the Brenner potential [9–11], as well as in a tight-binding quantum mechanical framework which is completely independent of the classical simulations [7]. We have also examined this model system with He, and found that also it can lead to bond breaking, albeit with a clearly lower cross-section.

In addition to the study of the dimer model system, we have carried out extensive simulations of H, D, and T bombardment of actual a-C:H material. The main results obtained can be summarized as follows. We have shown that the SCS mechanism leads to sputtering of small hydrocarbon molecules down to energies of about 2 eV, and that the sputtering yields obtained agree well with experiments [6]. We have also observed that the sputtering yields are highly sensitive to the detailed surface structure

[12], and that for high fluxes a H supersaturation can form on the surface, which can reduce the C sputtering by an order of magnitude [13]. These observations explain experimental results on the same systems. We have also examined the temperature dependence of the sputtering yield, offering a possible explanation to why the yield had a maximum at about 700–900 K [6] (although the so-called Küppers cycle [3] is certainly also active at these high temperatures). Most recently, we have found that even if 10 % of the bombarding particles are He, Ne, or Ar, with the *same* energy as the incoming H, the erosion yield does not change appreciably (more than 10 %) compared to the case of bombardment by H only [14].

Also, other groups have now carried out similar simulations of H bombardment of graphite and found essentially the same mechanism to be active [15–17]. All of this work focused on carbon due to its importance in fusion reactors. Since our argument for how the bond breaking occurs is a very generic one and does not require any particular features specific to carbon, however, it is natural to pose the question whether this mechanism can be important during the bombardment of other materials as well. Thus, we next discuss low-energy light ion bombardment of a metal carbide and a-Si:H.

SPUTTERING OF TUNGSTEN CARBIDE

The SCS mechanism cannot happen in appreciable amounts in metals, since it requires the presence of loosely bound atoms or molecules at the surface, that are only bound to the substrate by one or at most a few chemical bonds. Metals tend to favor atomic configurations where each atom has numerous nearest neighbors, making SCS unlikely. However, it is not obvious whether a mixed system with both metals and carbon can sputter chemically.

Using a recently developed potential model for the W-C-H system [18], we have examined the modification and erosion of tungsten carbide by incoming D ions. Simulations of the sputtering of pristine crystalline WC show only physical sputtering, with yields that agree well with experiments within the statistical uncertainties. Simulations of high-dose irradiation, where the change in the sample structure induced by each ion is taken into account, indicate that WC amorphizes during low-temperature ion irradiation. This leads to the formation of loosely bound carbon chains at the surface, which can erode by chemical sputtering. On the other hand, during prolonged irradiation preferential sputtering (physical and chemical) will lead to a strong W enrichment at the surface [19], and then naturally the chemically enhanced sputtering of C will be much reduced or even completely cease.

SPUTTERING OF HYDROGENATED SILICON

Method

We have also examined the low-energy H and He bombardment of a system with no carbon involved. We chose to study hydrogenated Si, because this material is of interest, for instance, in photodetectors and solar cells and it is frequently manufactured with plasma methods [20,21]. We used the Beardmore implementation of the Murty–Atwater Si–H interatomic potential [22]. The interaction of He atoms with other atoms was described by density functional theory-based pair potentials [23,25].

We manufactured a bulk amorphous hydrogenated silicon (a-Si:H) simulation cell by taking one of our existing a-C:H cells (with about 40 % H), scaling its size upwards by the difference in lattice constant of Si and diamond, and relaxing it with MDs. The temperature and pressure were scaled toward zero with the Berendsen method with time constants of $\tau_p = 0.3$ ps and $\tau_T = 1$ ps [26]. This way, the cell initially heated up to several thousands of Kelvins and then slowly cooled, allowing the structure to find a reasonable bonding structure of a-Si:H. After manufacturing this cell, we removed the periodic boundary conditions in the z direction and fixed the atoms in the bottom z layer, producing an open surface in the top z layer. The cell size was held fixed to prevent surface tension from causing artificial pressure relaxation effects, while the temperature of the cell was relaxed with a time constant of

$\tau_T = 0.6$ ps to allow for the surface to relax. The relaxation led to the evaporation of a few unbound hydrogens, which were removed from the system. We verified that the cell thus obtained produced a stable surface by heating it up to 600 K for 10 ps, without observing any additional H or Si evaporation. The final simulation cell had 708 atoms and a size of about 20.2 Å in each dimension. We note that in the case of the 100 eV H ions, the cell was clearly too shallow to contain the full H trajectory, and the 100 eV sputtering yield may be somewhat underestimated because of this.

After this, we commenced with bombarding the a-Si:H cell with 0.5–100 eV H or He ions, and counted the number of outgoing Si atoms or Si-containing molecules to obtain the Si erosion yield (higher energies than 100 eV could not be run because of the limited cell depth). We did not include electronic stopping in most simulations, but tested including it in a few H cases. This led to similar or possibly somewhat lower sputtering yields within the statistical uncertainties of ~30 %. For each ion energy, we simulated 10 000 sputtering events. We manually reran a few of the events leading to sputtering, monitoring the sputtering mechanism and verifying that the total energy is well conserved.

To obtain a point of comparison with a purely physical sputtering model, we also simulated the same bombardments of a-Si:H using binary collision approximation (SRIM) [27,28] in the full cascade mode. We set the a-Si:H density to be the same as in the MD, but otherwise used the default SRIM parameter values for, e.g., displacement and surface binding energies.

In our previous works, we have found that to obtain a statistically representative description of a macroscopic surface, it is necessary to simulate sputtering from simulation cells with different surfaces and obtain an average yield over these, or do an average over dynamically changing surfaces [6,14]. In this work, however, our aim is to simply examine *whether* SCS can occur also from Si-based materials. Hence, we examined only one simulation cell to obtain a qualitative answer to this question.

RESULTS

The erosion yields of a-Si:H obtained from our simulations are illustrated in Fig. 2. The data for hydrogen show how physical sputtering (the SRIM results) becomes insignificant at about 50 eV, while the chemical sputtering occurs down to 1 eV, and has a significant and almost energy-independent yield around 0.002 between 5 and 50 eV. This result is very similar to the experimental and simulated observations for a-C:H cited above.

The figure also shows that He can lead to sputtering of a-Si:H at energies down to 10 eV, clearly below those where physical sputtering is significant. In all the three cases where 10 eV He led to Si sputtering, the sputtered species was SiH₄, which shows that the erosion is of chemical rather than physical nature. Moreover, analysis of the atom trajectories showed that the He–Si interaction is not a direct collision. Instead, the He disturbed the chemical bonding environment around the Si by putting both Si and H atoms in motion, leading to bond breaking. The motion of the loose Si atom was so slow it had time to capture a fourth hydrogen before leaving the surface.

The reason that SRIM gives higher yields than MD for He bombardment at high energies is that the default SRIM parameters of displacement and binding energies are not in line with the MD energetics. Sputtering yields predicted by binary-collision approximation methods are well known to be highly sensitive to the parameter choices [29], and in this particular case we found that changing just the SRIM displacement energy parameter for Si from 15 to 20 eV changed the yield for 50 eV He by almost an order of magnitude. Changing the SRIM parameters to give agreement with MD would only increase the sputtering threshold energy in SRIM, and thus not affect our conclusion that MD gives a much lower threshold.

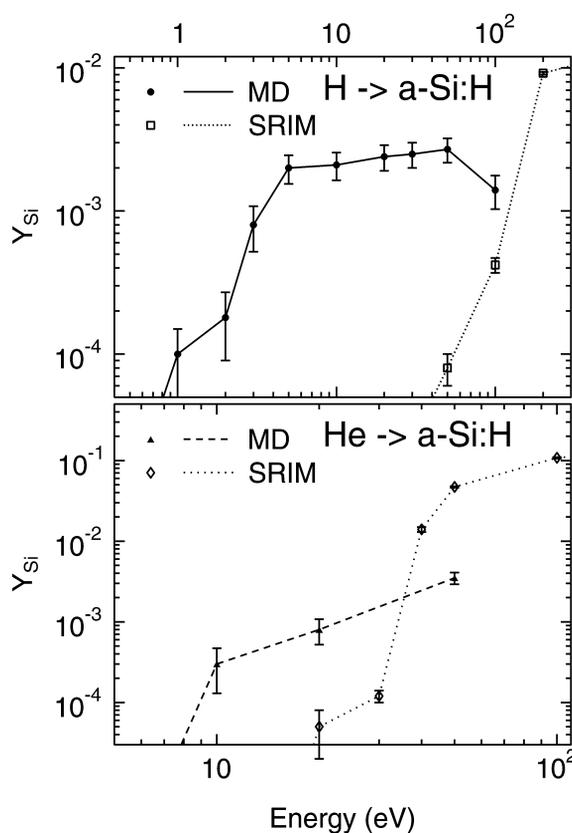


Fig. 2 Erosion yields of Si from a-Si:H as determined by MD and SRIM methods. The SRIM method does not describe chemical bonds at all and hence is representative of purely physical sputtering. The differences between the MD and SRIM results thus illustrate the importance of SCS.

Also, in the case of H bombardment of Si–Si bonds, the atom motion leading to the bond breaking was not always as simple as when a H atom enters the region between two Si atoms. One such case is illustrated and described in Fig. 3. Note that the process is endothermic, consistent with the description of an energy threshold for the dimer bond breaking and the observation that it has a kinetic energy threshold.

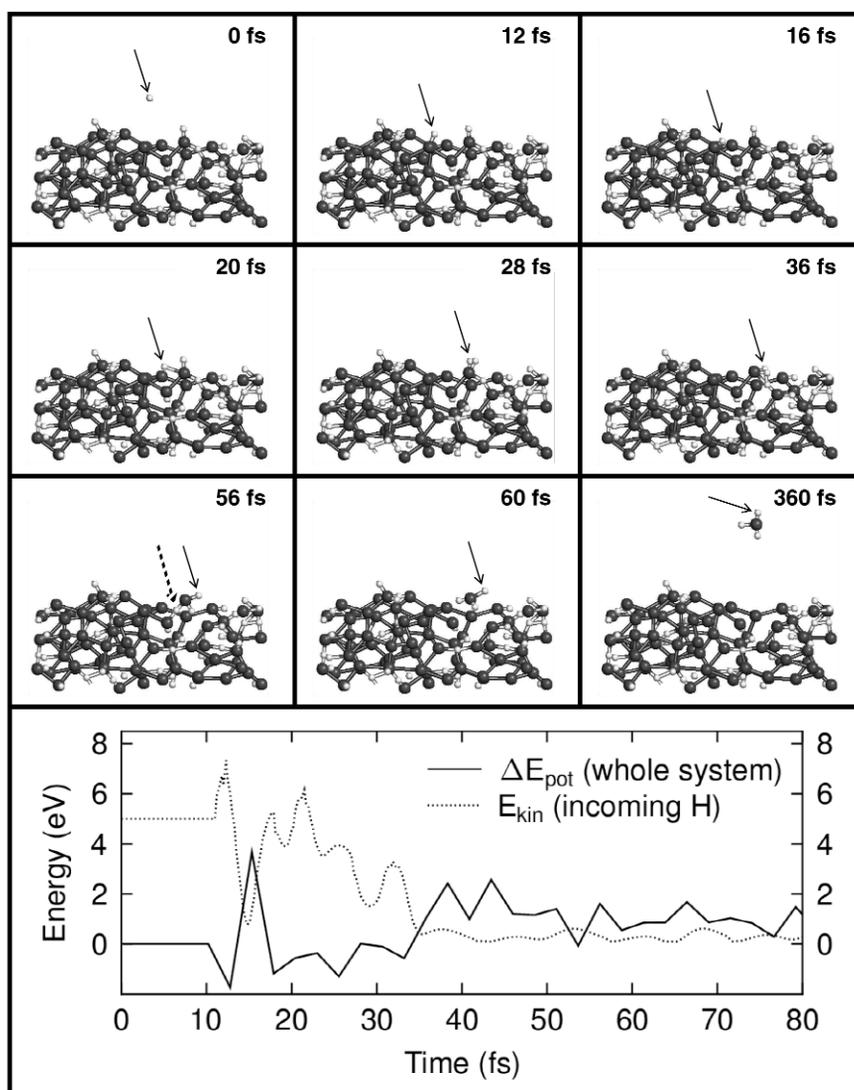


Fig. 3 Erosion of a SiH₃ species from a-Si:H by an incoming H. Upper part: small light spheres are H and the larger dark ones Si. The incoming H atom is always marked by the thin solid arrow. The incoming H is first scattered (12–16 fs) from one Si, changing its movement direction. It then interacts with a H in a loosely bound SiH₂ species (28 fs), making this and the other H in the SiH₂ rotate (28–56 fs). One of the H atoms originally in the sample then enters the space between two Si atoms (56 fs, thick dashed arrow), leading to swift chemical bond breaking. The lower part illustrates the energetics of the process. In the first scattering event (10–20 fs), the incoming H is slowed down and the potential energy rises, as expected for a binary collision process. During the bond breaking (30–60 fs), the incoming H transfers its remaining kinetic energy to the SiH₂ species, leading to bond breaking and an associated rise in the potential energy of the system. The final potential energy is higher than the initial one.

DISCUSSION

As discussed in the previous sections, the SCS is a kinetically activated, endothermic process which can lead to erosion of heavy atoms from covalently bonded materials. Its essence is that a light ion (H or He) penetrates at least partly between two covalently bonded atoms, pushing them apart and causing bond breaking. We have observed it to occur for both H and He irradiation, but it is very unlikely to occur for much larger atoms since these transfer much more kinetic energy to the sample atoms when penetrating a bond, making the process physical rather than chemical sputtering. As an example showing this, we consider the energy transfer from 20 eV ions in a binary collision to a Si atom with the impact parameter of 1.175 Å corresponding to the midpoint of a Si–Si bond. The energy transfer is calculated by numerical solution of the collision integral [30] using the Ziegler–Biersack–Littmark screening function [27]. While H transfers only 0.08 eV and He only 0.6 eV, C transfers 3.3 eV and Si 7 eV. Thus, the heavier ions could cause breaking of a Si–Si bond by a purely collisional mechanism without the need to consider the nature of the chemical bond.

Although the model system of the dimer shows a simple mechanism by which the erosion can occur, the discussion in the previous section illustrated that it can be more complex. As shown in Fig. 3, the atom penetrating a bond need not be the incoming ion, but can be the one that has received recoil energy from an incoming ion. This makes it possible that even heavy ions could, at least in principle, indirectly cause SCS via energy transfer to hydrogen. Further work would be needed to analyze whether this process could have a probability significant compared to physical sputtering. At higher energies, it is of course possible to have mixtures of physical and chemical sputtering, e.g., when a light ion transfers kinetic energy in a ballistic collision, while at the same time weakening a bond.

Finally, we addressed the relation of the SCS mechanism described in this paper to other erosion mechanisms previously discussed in the literature.

The SCS is not the same kind of chemical sputtering as that described by Winters and Coburn, since in that mechanism a particle weakens a bond which then can desorb [31]. In the current case, the bond breaks immediately. Of course, both mechanisms may be active simultaneously at high enough temperatures.

Since the SCS mechanism is endothermic and requires a kinetic energy above thermal ones, it is not etching in the traditional sense of using a chemical to remove parts of a material. However, nowadays the word “etching” is often used to describe any kind of process facilitating controlled removal of material. SCS can certainly be considered a variety of ion beam or sputter etching [32], and because it is most important at energies around 10 eV, typical of hyperthermal beams, it could well be considered a variety of hyperthermal beam etching.

We also compare the SCS mechanism to the extensively studied case of fluorine etching of Si. This process has a nonthermal reaction mechanism [33] similar to that of the SCS, and involves loosely bound SiF₃ surface species [34,35] in geometrically very similar configurations as the CH₃ and SiH₃ species observed by us. The fluorine etching can occur by a process known as nucleophilic substitution, which is exothermic by several eV and has an activation barrier of about 1 eV [34]. The SCS mechanism also has a comparable barrier, but is endothermic. Note also that the H-induced carbon erosion experiments are often in fact carried out with H₂ or H₃ ion beams [36,37], increasing further the endothermicity of the erosion.

Barone and Graves [38] have described the erosion of Si by F (or Cl) in terms of three mechanisms: (i) physical sputtering, defined as the etch product leaving the surface within 1.2 ps of the impact where the incoming fluorine is not part of the etched molecule, (ii) chemical sputtering by the Winters–Coburn mechanism, and (iii) direct abstractive etching (DAE), which is the case when the etch product leaves within 1.2 ps of the impact with the incoming fluorine. In SCS, the incoming H may or may not leave with the sputtered species. Hence, SCS falls within both of these definitions. For the reasons discussed above, however, we do not consider SCS as physical sputtering. Using the most general definition of DAE from [38] that an “incoming halogen (ion) abstracts a silicon from the surface”, the

SCS can be considered a variety of DAE. However, because etching is often understood to imply an energetically favorable process, we consider the term SCS with the word sputtering more descriptive.

In the surface science and catalysis literature, a mechanism in which an atom or molecule incoming on a surface directly combines with an adsorbed surface species leading to formation of a desorbed species in an exothermic reaction is called an Eley–Rideal mechanism [39]. Because the SCS is endothermic and can occur with the substrate atoms themselves, it is not an Eley–Rideal mechanism.

CONCLUSIONS

In conclusion, we have described in detail the SCS mechanism, which is an endothermal and athermal process which can lead to erosion of small molecules from covalently bonded materials by low-energy (~10 eV) H atoms and molecules as well as He atoms. It may thus be an important effect for H and He-containing plasma processing of materials. We also discussed the relation of this mechanism to previously described erosion effects, finding that using the most general definitions, it could also be called etching or an abstraction reaction. However, because SCS is energetically unfavorable and requires a kinetic energy above thermal ones, we argue that a name with the word “sputtering” is most descriptive.

ACKNOWLEDGMENTS

We are grateful to Prof. D. B. Graves for useful discussions regarding the abstraction reactions. The research was supported the Academy of Finland under project No. 202737, by Association EURATOM-TEKES, and by the M. Ehrnrooth foundation. Grants of computer time from the Center for Scientific Computing in Espoo, Finland, are gratefully acknowledged.

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