

## Reduced chemical sputtering of carbon by silicon doping

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Doping is a widely used method to enhance the properties of materials. Despite the recently increased understanding of the mechanisms of chemical erosion by low-energy hydrogen ions, the effect of doping on these types of processes is still not well understood. We study the erosion of Si-doped (0 – 30 at.%) carbon under 20 eV deuterium irradiation using molecular dynamics simulations. We show that the chemical sputtering of carbon decreases with increasing Si concentration. The reasons for the reduced sputtering yield lie in the longer Si–C interaction lengths and efficient dynamic rebonding of hydrocarbon species.

Carbon-based materials are widely used as protective coatings due to their hardness, excellent thermomechanical properties, and chemical inertness<sup>1</sup>. In modern fusion devices carbon-based materials (namely graphites and carbon fiber composites, CFCs) are used as plasma-facing components (PFCs), which are subject to extreme heat loads during the device operation as they are continuously bombarded by high particle fluxes, including low-energy hydrogen atoms and ions. It has been well established that even low energy ( $\leq 20$  eV) hydrogen bombardment of these materials can result in significant carbon sputtering<sup>2–6</sup>. Not only is the lifetime of the PFCs reduced, but the eroded species dilute and cool the fusion plasma. This leads to the extinction of the fusion reaction. Analytical models for the low-energy sputtering have been previously suggested<sup>7,8</sup> and our molecular dynamics (MD) modeling<sup>9,10</sup> has provided a detailed picture of the chemical sputtering mechanism relevant at these low energies.

Several elements, such as Si, B, Ti, V and W, have been proposed to be used as dopants to enhance the properties of the carbon materials<sup>11,12</sup>. Along with other enhanced PFC properties<sup>13,14</sup>, experiments with Si- and SiC-doped CFCs under low-energy hydrogen irradiation have shown reduced sputtering yields<sup>15–17</sup> compared with undoped carbon. But the uncertainties and scatter in the experimental data are large, emphasizing the importance of having a fundamental understanding of how the Si concentration affects the carbon sputtering. It is well known that composition and dose effects can affect *physical* sputtering yields in compound materials<sup>18</sup>. However, for the 20-eV D irradiation of Si-doped graphite no dose dependence of the sputtering yield was observed<sup>15</sup>. Using molecular dynamics computer simulations we now show how chemical effects (the length of a chemical bond and dynamic rebonding) can lead to a strong, dose-independent reduction in *chemical*

sputtering yields with increasing dopant concentration.

Since the carbon sputtering yields by hydrogen at energies  $\leq 20$  eV are of the order of  $10^{-3} - 10^{-2}$ , a force model capable of computing thousands of trajectories in a reasonable time is required. We employ a classical many-body force model for Si-C-H systems<sup>19</sup>, which takes into consideration non-local effects and provides a realistic description of bond forming and breaking. As the details on our modeling of hydrogen bombardment have been described elsewhere<sup>9,10</sup>, only the central aspects are presented here.

To model a dose-independent situation, the simulations were not cumulative<sup>20</sup>. An impact energy of 20 eV was used for the impinging deuterium. The energy was chosen to lie below the threshold of physical sputtering of graphite but high enough to result in significant chemical sputtering. The reason we used D instead of H in our simulations is that more experimental data is available for D irradiation at low-energies<sup>2,5,15,16</sup> for comparison with our results. Since the sputtering of Si- and SiC-doped CFCs mainly takes place at the amorphous matrix between the carbon fibers<sup>17</sup>, our simulation cells were created from a random network of D, C and Si atoms. The bonding geometry was optimized with annealing and pressure scaling<sup>21</sup> simulations. Si/(Si+C) fractions between 0 and 0.3 were used. The degree of deuteration in all the cells was chosen as the bulk saturation value of hydrogen in hard carbon structures at 300 K,  $D/(Si+C) \sim 0.4$  (Refs. 22, 23). The initial surface temperature was 300 K and the temperature was scaled to this value at the cell borders during the irradiation simulations.

The carbon atoms were mainly ( $\sim 75 - 80$  %) threefold-coordinated (C(3)) with some fractions of C(2) and C(4) sites. Si atoms were mainly Si(4) but fractions ( $\leq 10$  %) of Si(3) and Si(5) coordination defects were present in all the simulation cells. Irradiated covalently bonded materials are known to contain defects which

can be annealed only at high temperatures<sup>24,25</sup>. In agreement with that observation our simulations showed that coordination defects will be formed at the surface by low-energy deuterium bombardment. Hence, we felt confident that the structure obtained by our method could be used for the irradiation simulations.

We found that the surface microstructure of the Si-C-H network has a significant influence on the carbon sputtering yield. Hence, to obtain sputtering yields representative of macroscopic samples<sup>26</sup>, we have in the current work averaged the results for each Si concentration over 6 – 9 independently manufactured surfaces.

Figure 1 shows the carbon sputtering yields in our simulations as a function of the Si concentration. As in experiments<sup>3–5</sup>, carbon atoms were mainly sputtered in small  $C_yD_x$  hydrocarbons ( $y = 1,2,3$ ), including radical species. A decreasing trend of the carbon sputtering yield with increasing Si concentration is observed. Although no systematic experimental study on the effect of the Si concentration is available, a similar trend has been reported in the literature<sup>16</sup>.

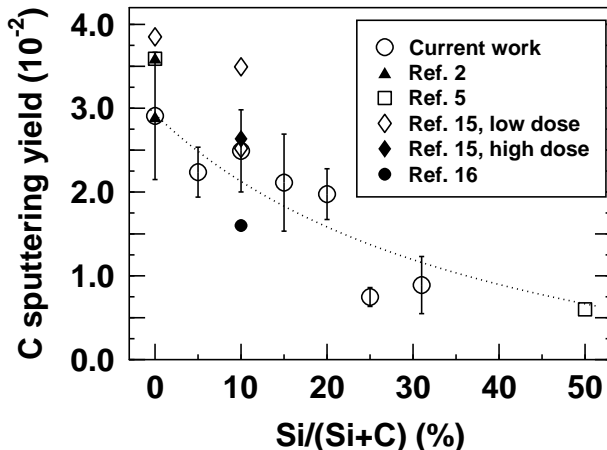


FIG. 1. Carbon sputtering yields as a function of the Si concentration. Experimental data for graphite<sup>2,5,15</sup>, 10 at.% Si-doped carbon<sup>15,16</sup> and SiC (Ref. 5) are also shown. The dotted line is a fit to our simulated data ( $\alpha = 3.6$ ).

As the yield decreases more strongly than the concentration of carbon atoms in the Si-C network, a fit of the form  $Y_n = Y_0 \times N_C / (N_C + \alpha N_{Si})$  was made to the simulated data.  $Y_n$  is the carbon sputtering yield for Si-doped ( $n$  at.%) carbon matrix, and  $Y_0$  (sputtering yield for undoped carbon) a fitting parameter.  $N_C$  and  $N_{Si}$  are the numbers of carbon and silicon atoms, respectively. The parameter  $\alpha$ , which describes the effect of silicon on the chemical sputtering, was chosen on the basis of our understanding of the swift chemical sputtering mechanism<sup>9</sup>. An initial choice was the ratio of the average volume occupied by a silicon and carbon atom,  $\alpha = 3.4$ , as calculated from the average C-C and Si-C

bond lengths in the simulation cells. The best fit for  $Y_0$  resulted in a value of 2.9. When  $\alpha$  was also chosen as a fitting parameter, values of  $\alpha = 3.6$  and  $Y_0 = 3.0$  were obtained. Both fits are in a good agreement with the experimental data (the latter case is shown in Fig. 1).

The Si sputtering yields were of the order of  $10^{-4}$  and increased with Si concentration. However, the number of sputtered Si atoms was always much lower than expected simply from the number of Si atoms in the Si-C network. This is explained by the weak energy transfer (maximum  $\sim 25\%$  of the impinging D energy) between Si and D atoms in collisional events<sup>27</sup> and by the high number of Si-Si/C covalent bonds for chemical bond breaking.

The reasons for the reduced chemical sputtering of C are not obvious, as typical Si-C bond energies are weaker than C-C bond energies<sup>28</sup>. On the other hand, the longer Si-C bond lengths decrease the transverse momentum transfer in bond breaking events<sup>9</sup>. We examined single bond breaking events with simple molecules  $SiD_3CD_x$  ( $x = 2,3$ ) and  $C_2D_4$ . Deuterium atoms with fixed kinetic energies (5 – 20 eV) were shot in the region between the central Si/C atoms in the molecules. The bond breaking probabilities for  $SiD_3CD_2$  and  $C_2D_4$  were very similar throughout the energy range considered, while the  $SiD_3CD_3$  species had an increased bond breaking probability at energies above  $\sim 10$  eV. Since the majority of the carbon atoms in our simulation cells were C(3), the explanation for the reduced C sputtering yields has to lie in an effect of Si atoms on the development of the impact cascade, and not on single bond breaking processes alone.

We analyzed in detail hundreds of bombardment events for various simulation cells. The ion penetration depths as well as the number of reflected ions from the cell were similar for all the Si concentrations. Furthermore, analysis of the ion energy loss during the surface penetration did not show any significant differences between the Si-C structures. The breaking of existing bonds and formation of new bonds was also examined for atoms which interacted with the impinging ions. We concentrated on the cases with the possibility of erosion, *i.e.* cases where a carbon atom in the bulk was displaced more than 1.0 Å from its initial position (thus excluding thermal motion) and coincided with a change in the bonding configuration of the same atom. We observed that a significant amount of carbon atoms had been bonded to Si sites.

As the simulation cells contained a fraction of threefold-coordinated silicon atoms Si(3), we considered the possibility of dynamic rebonding of  $C_yD_x$  species as an erosion-reducing mechanism. This means that a hydrocarbon species that is no longer bound to the Si-C network encounters an undercoordinated silicon or carbon site and rebonds to it.  $C_yD_x$  species moving towards the bulk surface could then be bound instead of sputtering away. The kinetic energies of the unbound species after the bond breaking are typically quite low ( $\sim 0.1$  eV) compared with the energy gain for the formation of Si-Si, C-Si, or C-C bonds ( $\sim 2 - 5$  eV). Hence,

provided that no steric hindrances for the bond formation exist, the reaction seems plausible.

The empirical Si-C-H potential energy function predicts the reactions  $-\text{Si}(3) + \text{CD}_x \rightarrow -\text{Si}(4)-\text{CD}_x$  ( $x = 0,1,2,3$ ) to be energetically favorable. This is not a large surprise as the bonding configuration of the undercoordinated Si atom becomes saturated. However, we also observed the formation of Si(5) coordination defects, originating from hydrocarbon species bonding to Si(4) sites. As this could be an artefact of the empirical model, a more detailed study was required. We considered the following reactions: (1)  $\text{CH}_3 + \text{SiH}_4 \rightarrow \text{CH}_4-\text{SiH}_3$ , (2)  $\text{CH}_4 + \text{SiH}_3 \rightarrow \text{CH}_4-\text{SiH}_3$ , and the corresponding cationic reactions (3)  $\text{CH}_3^+ + \text{SiH}_4 \rightarrow \text{CH}_4-\text{SiH}_3^+$ , (4)  $\text{CH}_4 + \text{SiH}_3^+ \rightarrow \text{CH}_4-\text{SiH}_3^+$ . The species on the left represent unbound hydrocarbons encountering bulk network Si centers (either Si(3) or Si(4)). The reactions were studied at the density functional theory (DFT) level using the B3LYP functional together with a SVP basis set, as implemented in TURBOMOLE<sup>29</sup>. The use of protium instead of deuterium as the hydrogen isotope is of no importance as the chemical reactions of the isotopes are identical. In all four reactions the compound configuration was energetically more favourable in comparison with the fragmented configurations. Although the energy gain for the reactions (2) and (4) was only about 0.2 and 0.9 eV, respectively, the formation of saturated molecules due to the swift chemical bond breaking is much less probable than the formation of radical species. Hence, the rebonding of small hydrocarbon species to Si sites, as studied with the reactions (1) – (4), seems possible.

A further study showed that a major factor for the reduction of chemical sputtering in our modeling is the long interaction range of the Si-C potential energy function. We constructed a modified version of the potential in which the maximum Si-C interaction range was shortened from 2.5 to 2.2 Å. The C and Si bonding configurations were unmodified after a short relaxation<sup>30</sup>. However, carbon sputtering yields obtained with the modified potential energy function were higher in almost all the test cases, up to by a factor of 3. This clearly shows the effect of the Si-C interaction range on the sputtering processes. As a side remark, it should be remembered that hydrocarbon species can be sputtered away *directly* from the surface. In this type of process the effect of silicon can be expected to be weaker as the unbound species can drift away from the surface unhindered, and the situation reduces to a similar case as was studied with simple molecules above.

In conclusion, we have studied the effect of Si doping on the low-energy irradiation of carbon by deuterium. The carbon sputtering yield was observed to decrease with increasing Si concentration, while the Si sputtering yields remained at least an order of magnitude lower than those of carbon. The reduction of carbon sputtering was shown to arise from the long Si-C interaction range. Dynamic rebonding of unbound hydrocarbon species to Si sites was shown to take place during the irradiation. Rebonding

reactions of small hydrocarbon species to Si(3) and Si(4) sites were shown to be energetically favourable.

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