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Suppression of carbon erosion by hydrogen shielding during high-flux hydrogen bombardment

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The erosion of carbon by intensive hydrogen bombardment has been recently shown to decrease sharply at very high fluxes ($\sim 10^{19}$ ions/cm^2 s). This effect cannot be explained by standard sputtering or erosion models, yet understanding it is central for selection of fusion reactor divertor materials, and formulation of sputtering models for high-flux conditions. Using molecular dynamics computer simulations we now show that the effect is due to the buildup of a high hydrogen content at the surface, leading to a shielding of carbon atoms by the hydrogen. [S0163-1829(99)50344-5]

The sputtering and erosion of atoms from surfaces by particle bombardment is significant in a wide range of materials physics experiments and applications, ranging from thin film growth and ion plating to understanding high-energy particle bombardment.[1–3] Standard models describing the sputtering and erosion of materials by ion bombardment assume that the sample composition remains constant during the bombardment, implying that the erosion yield per incoming ion is independent of the ion flux. Very recent experiments, however, show that during conditions of extremely high-flux hydrogen bombardment the erosion yield of carbon drops by at least an order of magnitude between fluxes of 10^{18} – 10^{20} ions/cm^2 s (Refs. 4 and 5). Since this carbon erosion effect is highly detrimental to fusion reactor operation, this surprising effect may be of crucial importance for the development of commercially viable reactors. Understanding it is also important for assessing under which other conditions conventional sputtering models may fail.

The carbon erosion is an inherently atomic-scale effect, and therefore atomistic computer simulations are ideally suited for obtaining a fundamental understanding of it. We use classical molecular dynamics (MD) techniques to simulate the bombardment of carbon-based divertor materials by hydrogen escaping the fusion plasma. The results show that the reason for the sharp drop in the carbon erosion yield at high fluxes is the buildup of a high hydrogen content within the first 1 nm from the surface. The high hydrogen content leads to a shielding of carbon atoms by hydrogen and hence a decrease in the cross section of collisions with carbon atoms. This effect can be expected to be present also in other materials under high-flux low-energy ion bombardment.

In tokamak-type fusion reactors the plasma is confined in a torus-shaped chamber by a magnetic field. Due to plasma instabilities some of it escapes the closed field lines and plasma particles collide with the first walls of the chamber. In order to control the escaped particles, this boundary plasma flux is directed towards two sets of divertor plates at the bottom of the torus with two intersecting magnetic field lines. Ion temperatures in the boundary plasma are much lower than in the actual core plasma, typically ranging from a few eV (high recycling conditions) to several tens of eV's (low recycling conditions).[6]

Since core plasma purity is critical in fusion operation, the choice of divertor material is very important. Impurities etched from the materials by boundary plasma interactions enter the core plasma, resulting in bremsstrahlung radiation which extracts energy from the plasma. This cools down the core plasma until the temperature decreases below breakeven conditions and the fusion is no longer self-sustaining.

Carbon- or hydrogenated carbon-based materials are the most promising candidates for a divertor material.[7] Since carbon has a low atomic number and high cohesion energy, both physical sputtering and chemical erosion from the divertor plates are reduced, and the low atomic number of the particles entering the plasma decreases the detrimental bremsstrahlung radiation. Continuing ion bombardment during the reactor operation eventually results in a distorted amorphous hydrogenated carbon (a-C:H) structure at the surface of the divertor plates, with a H:C ratio of about 0.4 (Refs. 8 and 9).

Recent experiments at several tokamaklike fusion reactor prototypes show that during hydrogen bombardment from the fusion plasma, the carbon yield drops by at least an order of magnitude between fluxes of 10^{18}–10^{20} ions/cm^2 s (Refs. 4 and 5). The effect is present for both H and D ions and both for low and high recycling conditions.

The conventional theory of physical sputtering[10] predicts that the sputtering yield is independent of flux, and hence cannot account for the effect described above. Theories for physical and chemical sputtering specific for carbon-based materials, meanwhile, have been quite successful at describing the energy and temperature, but not flux, dependence of the sputtering yield during hydrogen bombardment.[11] The analytical models of Roth and García-Rosales can explain a drop in yield for high fluxes *provided* the sample temperature exceeds 900 K (Ref. 5). In the experiments of Kallenbach *et al.* at the ASDEX upgrade tokamak, however, the drop in yield is observed even though the temperature is measured to remain below 360 K at the sample surface.[4] Hence no current model can account for the experimentally observed drop in carbon yield.[12]

Since analytical models have failed at describing carbon erosion during the high-flux conditions even qualitatively, we use another approach. We simulate the hydrogen bombardment effects using classical molecular dynamics simulations of ions[13] impinging on *a*-C:H. All hydrogen isotopes (H,D,T) are used in the simulation cells (for simplicity, in this paper we use *a*-C:H to denote cells containing any of the isotopes). To model the atomic interactions we used two versions of an empirical many-body potential developed by Brenner, parameter set II of the original potential[14] and a later modified formulation.[15] The Brenner potential has been parametrized with a large number of experimental data to describe hydrogen, simple hydrocarbon molecules, and carbon in both the diamond and graphite forms.

Since there is no single, unique *a*-C:H phase, there is neither a well-defined set of data which could be used to test the applicability of the Brenner potential for the present work. We did test the potential by first creating a simulation cell under conditions matching closely the ones used in a quantum mechanical simulation,[16] with the exception that the number of atoms in our cell was 500 instead of 76. Our pair correlation functions showed a good agreement with those found in the quantum mechanical simulations. Under simulations employing different pressure and temperature processing conditions the potential energies, cell densities and sp^3/sp^2 bonding ratios also behaved as expected on the basis of experimental data. The tests indicated that the Brenner potential can be used to describe *a*-C:H for the present purpose.

For computational reasons the simulation cell was kept fairly small, roughly the size of a 15 Å×15 Å×15 Å cube consisting of 500 atoms. This is large enough for simulations of impacts by low energy ($\lesssim 30$ eV) ions on the surface. A hydrogen-carbon ratio of 0.4 was chosen in the cell to match the experimental results. The cell was initially created as a bulk cell, after which a surface was created by removing periodic boundary conditions in the z direction, and the bottom layer atoms were fixed. The cell was equilibrated with long (30 ps) constant-temperature (300 K) runs after the opening of the surface to remove artificially broken bonds.

The plasma bombardment was modeled by creating a H, D, or T ion[13] outside an *a*-C:H cell, and assigning it a kinetic energy. Since energy distributions measured at divertor plates in tokamak-type fusion reactors often conform to the Maxwell velocity distribution,[7] the energy was selected randomly within this distribution for some root-mean-square (rms) energy. In the present study we used rms energies of either 1 eV or 10 eV, corresponding to the experimental high-recycling conditions. The ion was assigned a velocity towards the surface with a random off-normal angle between 0° and 20° and a random twist angle. The initial position was chosen so that the incident ion would not impact on the cell too close to the borders, where the temperature was scaled to 300 K to match the experimental value. More details on the general principles of our surface bombardment MD simulations are given in Ref. 17.

We performed three main sets of simulation runs: (1) cumulative ion bombardment of the *a*-C:H surface; (2) noncumulative bombardment of supersaturated[18] and unsaturated *a*-C:H surfaces; and (3) outgassing simulations of the supersaturated hydrogen content that had built up on the cell surface in the cumulative simulation runs. In the cumulative runs (1) an ion was shot on the surface and the cascade development was followed for 2 ps, after which another ion was shot *on the surface produced in the previous event*. In the noncumulative runs (2) the same initial cell was used for each ion event. This cell was taken to be either a virgin (unsaturated) *a*-C:H cell, or a supersaturated cell produced in the cumulative runs after at least 1000 bombardment events.

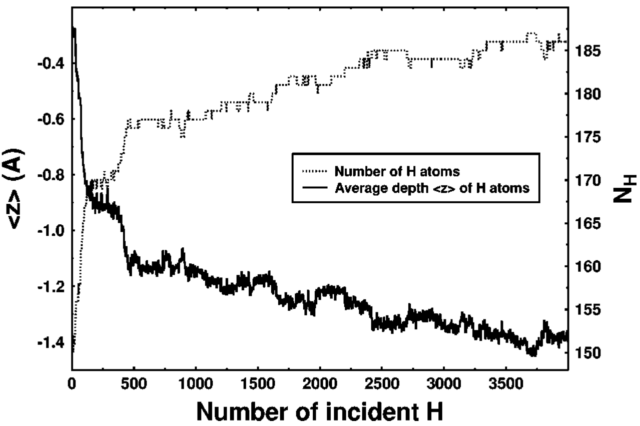

FIG. 1. The number and average z coordinate (depth) of the hydrogen ions in a cumulative run of H bombardment of *a*-C:H. The surface of the cell was at about -6.5 Å and the number of hydrogen atoms at the start of the simulation run was 151. The figure shows a fast hydrogen buildup on the surface leading to supersaturation.

In the first cumulative simulation runs the cell was impinged on by hydrogen with a rms kinetic energy of 1 eV. The high rate of ion incidence (1 ion/2 ps) led to hydrogen buildup on the cell surface, see Fig. 1. The hydrogen content first increased strongly, but after about 500 impinged ions the content starts to saturate. Between 2000 and 4000 ions the content increases only very slightly. The small increase seen in Fig. 1 results from H-H replacement collisions driving H atoms into unsaturated regions deeper in the *a*-C:H cell.

At the start of the cumulative simulations the predominant hydrogen erosion mechanism was ion reflection from the surface. As the buildup increased, ion reflection decreased and sputtering of hydrogen molecules became more and more frequent. The hydrogen atoms on the surface were loosely bound, with binding energies of about 2.2 eV. Although the impinging ions had very low kinetic energies, they were energetic enough to break hydrogen-carbon bonds and capture hydrogen atoms. Nevertheless, the flux was high enough for the buildup to result in saturation of the hydrogen content on the surface as well as a few Å under it (Fig. 1). The impinging hydrogen ions did not penetrate very deep into the cell. Out of the incident ions still residing in the simulation cell at the end of the simulation, 43% were below the original location of the surface, and only 8% were more than 2 Å below the original location of the surface.

No carbon or hydrocarbon sputtering was seen in the 1 eV H simulations. In 10 eV cumulative runs with impinging H and T ions some carbon erosion was observed, but otherwise the hydrogen buildup behavior was similar to that described above.

The noncumulative simulations gave us more precise probabilities for the different erosion mechanisms. A dramatic difference in the carbon yield was observed between

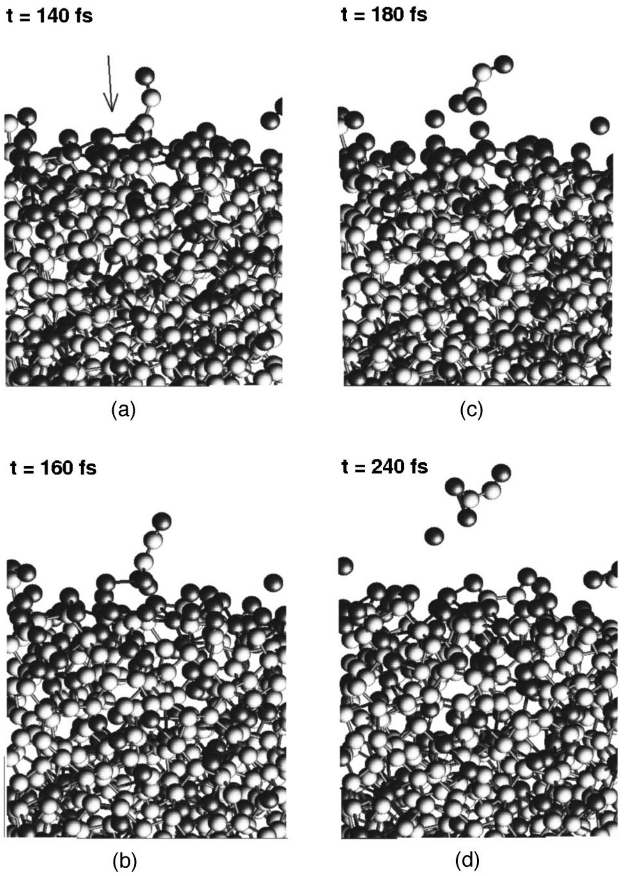

FIG. 2. Illustration of hydrocarbon molecule sputtering from an unsaturated *a*-C:T surface by an incoming T ion. The initial movement direction and impact point of the ion is indicated by the arrow. The light spheres represent carbon atoms and the darker ones T atoms. In the first slide the T ion has entered the sample and is interacting with a carbon chain. It breaks a carbon-carbon bond, leading to the formation of a C_2 compound bound only to tritium atoms. The next three slides (160, 180, and 240 fs) show how the C_2T_3 molecule leaves the sample, along with a nonbonded T atom (Ref. 22).

bombardment of unsaturated and supersaturated *a*-C:H cells. The carbon yield for the unsaturated surface was ~ 0.01, while for the supersaturated surface it was only ~ 0.001. This reduction by an order of magnitude is due to the high hydrogen content leading to a decreased carbon collision cross section, namely a shielding of carbon by the hydrogen atoms.

In most of the noncumulative simulations we used tritium cells and ions. From the unsaturated surface the carbon was etched away as simple CT_x (46%) and C_2T_x (46%) hydrocarbons along with a small fraction (8%) of single carbon atoms (cf. Fig. 2). For the supersaturated surfaces the total carbon yield consisted of only 3 molecules: two CT_x molecules and one C_2T_x molecule.

Reflection of the incident ion dominated T sputtering with both unsaturated and supersaturated surfaces. The tritium yield per incident ion with an unsaturated surface was 0.54 of which 65% were reflected incident ions and 26% sputtered T_2 dimers. For a supersaturated surface the tritium yield was much higher, very close to 1.0, and the fraction of reflected ions had decreased to 47% while sputtering of T_2 molecules had increased to 45% of all the etched tritium.

Although some H isotope effects were observed in the bombardment simulations, the effects were relatively small and not consequential for the conclusions of this paper. They will be discussed in detail elsewhere.[19]

The drop of an order of magnitude in the observed C erosion between a virgin and H-supersaturated[18] *a*-C:H surface is a likely explanation to the experimentally observed decrease in the erosion yield. The reason to the sharp drop is the decreased carbon collision cross section at a surface which has obtained a temporary supersaturation of H atoms due to the extremely high flux involved.

This effect is somewhat similar to the formation of self-sustaining coatings during ion bombardment by segregation of a binary alloy or bilayer.[20] In both cases a low-*Z* surface coating is formed, which suppresses the sputtering of a higher-*Z* element deeper in the sample. But the mechanism by which the low-*Z* coating forms is fundamentally different in the two cases. In our case the shielding layer is formed by the bombarding ions themselves, rather than by segregation by one of the sample elements as in the previously described effect.[20]

During thin film growth sputtering yields have in some cases been observed to depend on the rate of particle deposition,[1] which is analogous to the effect observed here in that one of the two bombarding beams appears to form a thin surface supersaturation decreasing the sputtering of the other ion species. Since the material characteristics and bombardment conditions are quite different, however, and no widely applicable theory for the effect of particle deposition rates on sputtering yields exists, the growth effect cannot be directly used to understand the drop in yield of issue here. In fact, this simulation study illustrates that MD methods can be very useful for understanding sputtering and growth effects in systems with anomalous surface composition.

Our noncumulative simulations of H bombardment do not correspond to any given flux, but to the two extreme ends of possible fluxes. The runs with H bombarding the unsaturated surface correspond to very low fluxes, where all supersaturated H atoms at the surface have time to outgas (desorb thermally) before another ion hits the same sample region. On the other hand, the runs with H bombarding a supersaturated surface correspond to very high fluxes, where the supersaturated surface hydrogen does not have time to outgas significantly. The cumulative simulation runs correspond to a flux of 2×10^{25} ions/cm^2 s. Simulations of lower fluxes would require a cumulative run with a longer time interval between consequent incident ions. The fluxes used in experiments[5] would require intervals of the order of microseconds, which is a far too long time scale for MD simulations. In the remainder of this paper we will, however, present an indirect means of assessing the flux dependence of our results.

The correspondence of our result to the experimentally observed drop in yield observed at fluxes of about 10^{19} ions/cm^2 s could be determined by finding the rate at which the supersaturated hydrogen content outgasses from the sample. The drop from a high erosion yield to a lower one will occur around the flux where the outgassing flux equals the incoming hydrogen flux.

To study the outgassing rate we simulated supersaturated *a*-C:H cells over long time scales ($\sim$1 ns) at different temperatures, without any ion bombardment. This allowed us to obtain the outgassing rates of the high hydrogen content at the surface. At high temperatures ($\gtrsim$2000 K) we observed a significant amount of both H and C erosion, and some erosion at temperatures between 700 and 2000 K. At room temperature no H erosion was observed within the time scale of the MD simulations, hence we were not able to obtain a statistically significant number for the outgassing rate. We can, however, give an upper limit of $\sim 10^{22}$ atoms/cm^2 s for the outgassing rate of the supersaturated hydrogen.

The diffusion of the supersaturated H at the surface into the sample was estimated to be utterly negligible ($D \sim 10^{-27}$ cm^2/s) at room temperature based on experimental diffusion constants from Ref. 21.

Based on the upper limit of the H outgassing rate and diffusion estimate we estimate that at room temperature the saturation and shielding effect described in this paper will still be present at fluxes as low as $\sim 10^{22}$ ions/cm^2 s, and possibly much lower. Experimentally the drop of about an order of magnitude in carbon erosion yield is observed at fluxes between 10^{18}–10^{20} ions/cm^2 s (Refs. 4 and 5). Thus the shielding effect observed in our MD model occurs at fluxes not very far from the experimental flux range. The simulated absolute carbon yields and drops in the yield are quite similar to the experimental values. Hence our results strongly indicate that the shielding effect described in this paper explains the experimental drop in yield.

The shielding effect has implications for reactor material development. Although the outgassing of H increases with increasing temperature, the equilibrium saturation concentration of H decreases.[9] Therefore, the divertor plates exposed to a high flux density ($\sim 10^{19}$ ions/cm^2 s) can be expected to be supersaturated even at higher temperatures, which leads to a decrease of carbon sputtering. Hence, the effect may increase the lifetime of the divertor significantly. Furthermore, since H reflection increases at supersaturated surfaces, the supersaturation during tritium bombardment may also decrease the probability of T entering deep in the sample, and thus decrease the harmful inventory of radioactive T.

In conclusion, we have shown that the experimentally observed decrease in carbon erosion from *a*-C:H during very high-flux low-energy H bombardment is due to the buildup of a high H content at the surface. The high H content leads to the shielding of carbon atoms from new incoming H ions, and thus a decrease of roughly an order of magnitude in the C erosion yield. The results also demonstrate that for extremely high fluxes standard sputtering models are not necessarily reliable since they do not account for temporary supersaturation of material at the surface.

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[1] J.M.E. Harper, J.J. Cuomo, and H.T.G. Hentzell, J. Appl. Phys. **58**, 550 (1985).

[2] G. Carter and D.G. Armour, Thin Solid Films **80**, 13 (1981).

[3] R. S. Averback and T. Diaz de la Rubia, in *Solid State Physics*, edited by H. Ehrenfest and F. Spaepen (Academic Press, New York, 1998), Vol. 51, pp. 281–402.

[4] A. Kallenbach *et al.*, Nucl. Fusion **38**, 1097 (1998).

[5] J. Roth and R.-C. Garcia, Nucl. Fusion **36**, 1647 (1996), and references therein.

[6] R. Schneider, Europhys. News **29**, 215 (1998).

[7] J. Küppers, Surf. Sci. Rep. **22**, 249 (1995).

[8] J. Roth *et al.*, J. Nucl. Mater. **93&94**, 601 (1980).

[9] B.L. Doyle, W.R. Wampler, and D.K. Brice, J. Nucl. Mater. **103&104**, 513 (1981).

[10] P. Sigmund, Nucl. Instrum. Methods Phys. Res. B **27**, 1 (1987).

[11] N. Itoh and Y. Horino, Nucl. Instrum. Methods Phys. Res. B **28**, 264 (1987).

[12] A. Kallenbach *et al.*, J. Nucl. Mater. **266-269**, 343 (1999).

[13] The classical MD simulations cannot take account of the charge state of atoms. Here we use the term ion to denote the incoming particle regardless of its charge state, and the term atom to denote any particle in the sample or sputtered out from it. The lack of charge states is not expected to affect the main results of the paper significantly.

[14] D.W. Brenner, Phys. Rev. B **42**, 9458 (1990).

[15] D. W. Brenner (private communication).

[16] G. Galli, S. Iarlori, and O. Martini, Phys. Rev. B **49**, 7060 (1994).

[17] J. Tarus, K. Nordlund, A. Kuronen, and J. Keinonen, Phys. Rev. B **58**, 9907 (1998).

[18] By supersaturation we mean in the present context hydrogen contents in *a*-C:H significantly higher than the experimentally observed equilibrium ratio of 0.4.

[19] E. Salonen *et al.* (unpublished).

[20] K. Morita, H. Ohno, M. Takami, and N. Itoh, J. Nucl. Mater. **128&129**, 903 (1984).

[21] E. Vainonen *et al.*, J. Appl. Phys. **82**, 3791 (1997).

[22] A GIF animation illustrating the erosion event is available on the World Wide Web at http://beam.helsinki.fi/demos/hcerosion.html