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A molecular dynamics study of diamond exposed to tritium bombardment for fusion applications

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ABSTRACT

Diamond, with its low atomic number and high thermal conductivity, is being assessed as a possible plasma facing material within a fusion reactor. Molecular dynamics simulations using the AIREBO potential were performed simulating the exposure of diamond to a plasma in conditions similar to those of the divertor region of a tokamak. Diamond surfaces at temperatures of 300 and 600 K were bombarded with 15 eV tritium at a high flux (10^{29} ions m^{-2} s^{-1}). A layer-by-layer etching process was observed which, with the lack of any tritium diffusion though the remaining diamond structure, was responsible for limiting damage, and thus tritium retention, to the top 4–5 diamond layers. Analysis of this damaged region also showed a large amount of residual structure suggesting that bombardment below the physical sputtering threshold (~30 eV) may not lead to amorphisation of the surface.

1. Introduction

In a tokamak fusion reactor plasma is magnetically confined within a vacuum. This isolates it from the surrounding environment and protects both the reactor against damage and the plasma from contamination. The inner wall of the reactor will be made of different plasma facing materials exploiting various strengths where appropriate. Necessary removal of fusion waste, and thus direct contact with the plasma, is limited to a region known as the divertor. It is expected that the divertor of the International Thermonuclear Experimental Reactor (ITER) [1] will be exposed to incident hydrogen isotopes of energies about 15 eV and at fluxes of the order 10^{24} ions m^{-2} s^{-1} [2]. These high fluxes are typically beyond the upper limit of experimental study and so computer modelling plays an important role in understanding erosion mechanisms.

A criterion for divertor material selection is exceptionally good thermal properties. For this reason tungsten and carbon, typically in the form of graphite or carbon fibre composites (CFC), are commonly used in and around divertor regions. Carbon may be preferable over tungsten due to its low atomic number, meaning it would radiate less heat as a plasma contaminate. Carbon does however have a major drawback in that it is highly reactive with hydrogen which can lead to tritium retention issues [3]. Simulations have primarily focused on sputtered yields from amorphous hydrocarbon surfaces at varying levels of hydrogenation and temperature [4–6] because surface structure is not expected to survive the harsh divertor conditions.

Diamond has been suggested as a possible plasma facing material [7] due to its high thermal conductivity and strong covalent bonding, although it is not currently widely accepted. This is largely due to fears of graphitisation or amorphisation at high temperatures and the potential for high levels of tritium accumulation. However, recent experimental evidence suggests that nano/microcrystalline diamond surfaces might survive tokamak conditions even better than graphite [8,9]. In this paper we use molecular dynamics calculations to examine the tritium retention and etching mechanism during the bombardment of a diamond surface at high fluxes.

2. Methods

The molecular dynamics package DL_POLY_3 [10] was used to simulate bombardment of a diamond surface with tritium. It was decided to use the Tersoff-Brenner-like AIREBO potential [11] in evaluating C–C, T–T and C–T interactions. This empirical bond-order potential is specifically parametrised to model the complex bonding involved in various hydrocarbon molecules. The consideration of varying bond strengths depending on the bond-hybridisation of neighbouring atoms is particularly important for studying the damage in diamond. It was decided to use the AIREBO potential without its long-range component which is especially useful in modelling the inter-molecular forces in hydrocarbon gases. This was due to the computational cost of using the full AIREBO and was found to have little impact in this study.

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Three crystal orientations in the perfect diamond tetrahedral configuration were initially considered, exposing the conventional diamond (100), (110) and (111) planes as surfaces in the z-direction. These initial simulation cells were constructed of 16,000, 16,896 and 15,552 carbon atoms, respectively, and of dimensions approximately $65 \times 65 \times 20$ Å^3. They were periodic in the x–y plane with open boundary conditions in the z-direction effectively creating two surfaces, the lower of which was frozen to a depth of 4 Å and only the upper was exposed to bombardment. A Langevin thermostat [12] was used to stochastically scale the velocities of carbon atoms within 4 Å of the cell edges in the x–y plane to the desired substrate temperature. Surface bombardment was restricted to no closer than 2 Å to this velocity scaled perimeter resulting in an average bombarded surface of dimensions 59×59 Å^2. This method of regulating the cell temperature was chosen to allow incident energy to defuse out of the system without artificially scaling the velocities of atoms directly involved with surface reactions. Simulations were carried out for substrate temperatures of 300 and 600 K. The simulation cells were initially prepared by gradual heating from 10 to 300 K and 600 K over increments of 5 ps and 34 K, using a constant pressure (NPT) ensemble.

Tritium was modelled using hydrogen parameters but with three times the proton mass. The term ion is used in this paper in reference to the incident tritium even though charges are not explicitly modelled. Each incident tritium was introduced to the system at a height of 10 Å above the surface with a kinetic energy of 15 eV. Impact site co-ordinates were selected randomly, as were off-normal incident angles in the range $0° < \theta < 80°$ (the azimuthal angle was completely randomized). A velocity-Verlet integration algorithm [13] with time-steps of 1 fs was used and an interval of about 0.3 ps was chosen between incident impacts, which corresponds to an ion flux $\sim 10^{29}$ ions m^{-2} s^{-1}. Material was considered as sputtered or reflected if it was 10 Å above the surface at the end of each 0.3 ps run and was removed from the simulation. At each substrate temperature 18,000 cumulative impacts were executed, equivalent to a total simulation time of 5.4 ns and a fluence of about 6×10^{20} ions m^{-2}.

3. Results and discussion

During the course of cumulative bombardment the ideal diamond surface gradually became damaged. The nature of this damage was found not to be sensitive to diamond lattice orientation. For example, no deeper tritium penetration was found for the (110) surface where the original diamond (111) planes are perpendicular to the surface. These (111) diamond planes preferentially form graphitic layers given enough energy, and since tritium is otherwise poorly soluble in diamond, they could reasonably be expected to facilitate the greatest amount of tritium transport. Instead it was observed that a fairly constant level of damage was sustained for all three orientations and so only one surface, the (110), will be referred to in examples through the rest of this paper. The exact dimensions of the bombarded area of the (110) surface were 48.4×56.3 Å^2 corresponding to a flux of 1.038×10^{29} ions m^{-2} s^{-1}.

At both temperatures the damage sustained by the diamond was initially gradual as the surface lost its ideal structure. As hydrocarbons began to sputter, more vacant sites became available which were chemically receptive to the incident tritium. Then from about 6000 tritium onwards (fluence of about 20×10^{19} ions m^{-2}) the level of tritium retention began to level-off, where incident tritium was balanced by the rates of tritium reflection/desorption and hydrocarbon sputter (Fig. 1).

During bombardment hydrocarbons were chemically sputtered, progressively etching away the diamond. Fig. 2 shows the steady-state erosion of carbon from the surface. After the first initial 6000 ions the depth of the retention/damaged layer was consistently confined to about 8 Å (including protrusion above the original surface level) leaving a relatively undamaged diamond structure below (Fig. 3).

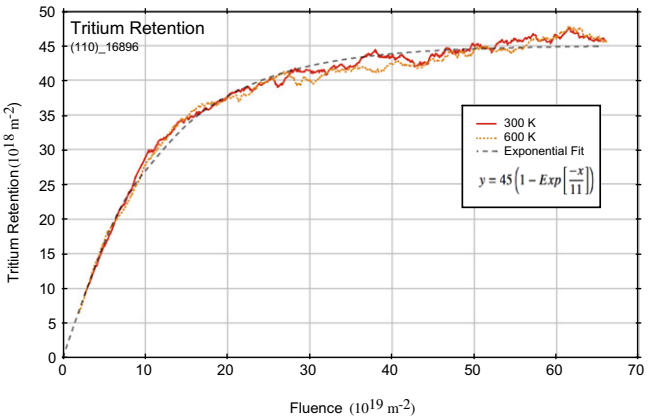

Fig. 1. Tritium retention of the (110) surface during bombardment.

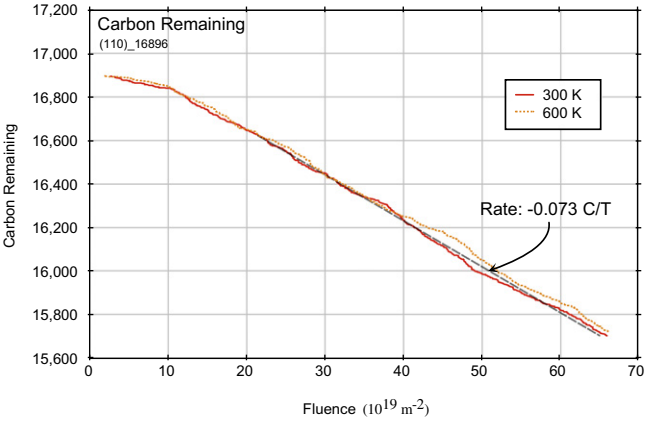

Fig. 2. Carbon remaining of the original 16896 C atoms during bombardment. Both temperatures have a similar erosion rate of about 0.073 carbon atoms for every incident tritium ion.

Fig. 4a shows the atom depth profile following bombardment with 18,000 ions at 600 K. The carbon peaks represent ordered diamond (110) layers of separation about 1.2 Å. The concentration of carbon is lower in the retention region, but the remaining carbon is still strongly centred about original diamond positions. Interestingly too, the retained tritium form peaks approximately 0.5 Å below those of the carbon, further indicating residual structure following bombardment. Fig. 4b is a depth profile of carbon atoms

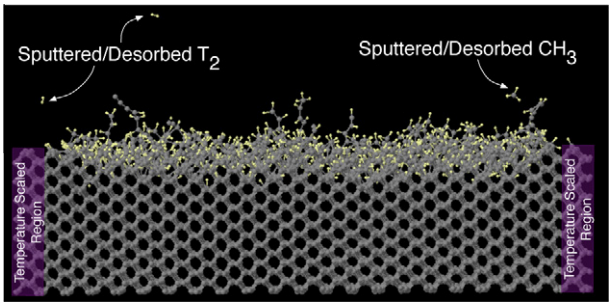

Fig. 3. Damaged (110) surface at 600 K after bombardment with 9000 T. Grey and yellow atoms represent carbon and tritium, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

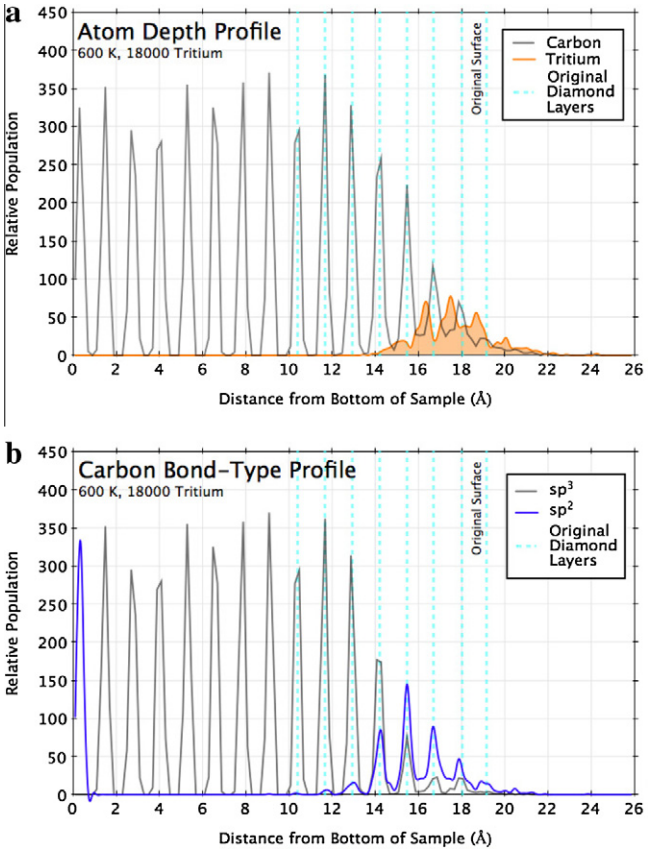

Fig. 4. (a) (1 1 0) surface atom depth profile following bombardment the with 18,000 T at a substrate temperature of 600 K. Tritium retention builds in-between diamond layers and at a depth of about 5 Å below the original surface level. (b) A similar plot, but of carbon bonding type. Damage-region carbons generally remain in original diamond positions despite preferentially forming sp^2-like bonds with other carbon atoms and/or retained tritium. Both profiles are taken for atoms 4 Å away from the temperature scaled region, that is 2 Å within the bombarded area.

only, distinguishing between atoms with four or three nearest neighbours (either other carbon atoms or tritium) interpreted as sp^3 and sp^2 bonding, respectively. Highlighted here is that as carbon atoms are eroded, adjacent carbon atoms remain roughly in their original positions. The number of atoms with two or one nearest neighbours only was negligible, demonstrating that even with a preference to form sp^2 bonds, remaining carbon atoms retain their original diamond positions.

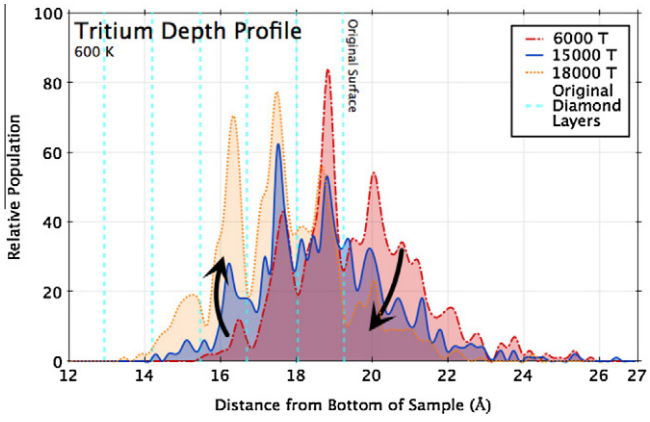

Fig. 5. Tritium retention of the (1 1 0) surface with time. Tritium builds in-between diamond layers and penetrates deeper into the structure only as upper layers are completely eroded. This layer-by-layer process limits tritium retention and preserves the diamond structure immediately below the damaged region.

The strong diamond structure immediately below the retention region can be explained by examining how this damage develops with time. Fig. 5 shows the build-up and erosion of tritium with time. Tritium is able to penetrate deeper only as upper layers are eroded but is still generally confined to inter-layer positions as much of the diamond structure remains. The activation energy for diffusion of H in diamond has been reported to be around 1.9 eV [14], therefore we would not expect to see diffusion on this simulation timescale. The gradual layer-by-layer erosion observed here confines retention and structural damage to the top four to five diamond layers only.

4. Conclusions

Recent experimental evidence has reported that on exposure to a plasma, diamond will form a thin amorphous hydrocarbon layer at the surface above a surviving diamond structure [15]. Results of the simulations presented here concur that although material is eroded, the damage due to low energy (15 eV) bombardment is confined to the surface. We also propose that the depth of this damage remains roughly of a constant thickness as diamond layers are successively eroded. This layer-by-layer mechanism is responsible for limiting the tritium retention to what the damage region can accommodate in satisfying carbon sp^2 bonding and thus for preserving a diamond structure below. We also suggest that what Porro et al. [15] identified as an amorphous layer based on Raman spectroscopic observations of sp^2/sp^3 concentrations could still in fact retain a certain amount of the original diamond structure (Fig. 4b).

Limiting structural damage of the diamond lattice to near the surface will mean that the exceptional thermal properties for which diamond would be a desirable plasma-facing material would remain for the bulk of the material. Specifically, the rapid transfer of heat away from the surface would help limit further thermally induced structural damage such as graphitisation or amorphisation.

Acknowledgement

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