Generation of Dust Seeds by Sputtering of Carbon-based Plasma Facing Materials under Low-energy H/D/T Ion Bombardment

Masashi Yamashiro* and Satoshi Hamaguchi
Center for Atomic and Molecular Technologies, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suits, Osaka 565-0871, Japan
E-mail: hamaguch@ppl.eng.osaka-u.ac.jp

Abstract: Sputtering properties of graphite and amorphous carbon substrates by hydrogen (H), deuterium (D), and tritium (T) at low incident energies have been studied with the use of classical molecular dynamics (MD) simulations. The sputtering simulations used here are accumulative in the sense that the surface modification due to impinging species are self-consistently taken into consideration. The simulation results indicate that a high level of H/D/T dose accumulation on the top surface is prerequisite for the formation of relatively large-sized sputtered hydrocarbon products. Especially significant isotopic dependence of sputtering yields has been observed at the accumulation dose over 10^{16} cm^{-2}, which is qualitatively consistent with some of the earlier experimental results.

1. Introduction

Low energy ion impact (with the injection energy being typically less than 50 eV or so) on the wall materials of a magnetic confinement fusion device such as a tokamak can generate a significant amount of sputtered species that may grow into dust particles through agglomeration in the gas phase or contaminate the hot core plasma. In this work, we have studied sputtering properties of graphite and amorphous carbon substrates due to hydrogen (H), deuterium (D), or tritium (T) ion bombardment at low energies using classical molecular dynamics (MD) simulations [1-4].

2. Molecular Dynamics Simulations for Plasma Surface Interaction

In classical MD simulations, the motion of each atom is followed as a function of time by the integration of the equation of motion. The classical interatomic potentials that we used in this work are Brenner-type multi-body potential functions [6] with weak Van der Waals interactions. The interatomic potential functions for H, D, and T are assumed to be the same and therefore, in our MD simulations, the only factor that differentiates them is their masses.

For the application of MD simulations to the study of plasma surface interaction, a special care to emulate the realistic system using limited simulation resources is in order. In our simulations, the substrate is represented by a collection of model atoms arranged in a rectangular parallelepiped with typically a few nm in each side and maintained at thermal equilibrium at a given temperature. For example, in the case of graphite used in our simulations, the model substrate consists of several graphene sheets thermalized at 300K, as shown in Fig. 1(a). The typical surface area of a model substrate that we used in this work is $2.0\times2.1 nm^2$. The graphene sheets are bound via Van der Waals interactions. The periodic boundary conditions are imposed in the horizontal directions of the model substrate, so that the simulation cell represents an infinitely large flat surface and its subsurface region. The bottom layer of the model substrate is fixed in time, meaning that they do not move during the simulation and serve as an anchor for the model substrate. Without the anchor

---

*present address: College of Industrial Technology, Nihon University, 2-11-1 Shin-ei, Narashino, Chiba 275-8576, Japan.

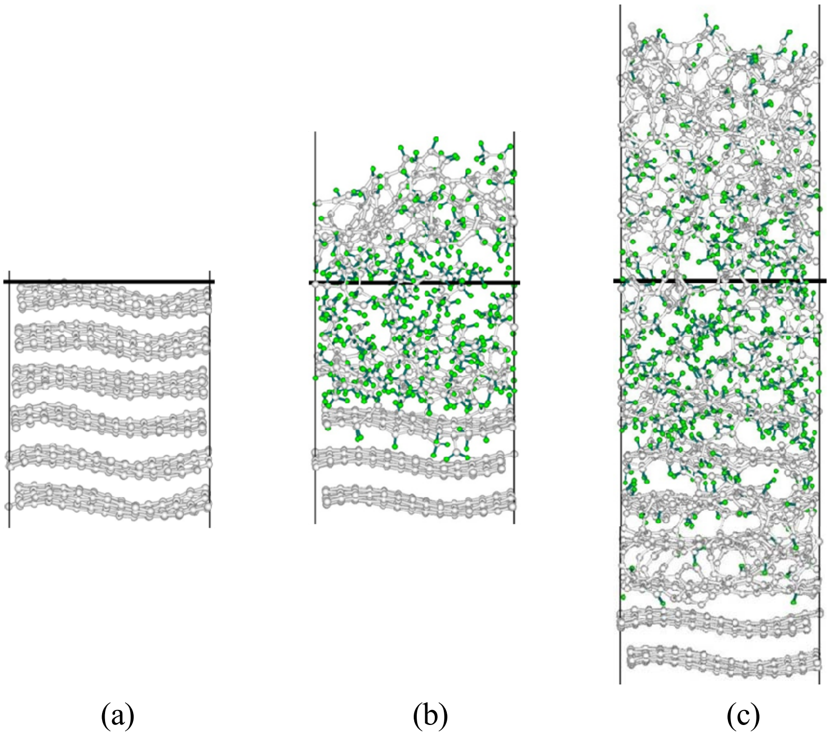


Fig.1: Surface morphologies obtained from atomic hydrogen (H) injection simulations for a graphite substrate. (a) The initial substrate of 1.72 x 2.13 nm^2 in area. (b) The substrate after 1.36 x 10^{17}/cm^2 fluence of 25eV H injections. (c) The substrate after 1.36 x 10^{17}/cm^2 fluence of 50eV H injections. The white and green spheres represent C and H atoms. The solid horizontal lines indicate the position of the initial top surface.

layer, the model substrate would move downward as a whole when it is subject to ion bombardment.

In the simulations presented in this article, H, D, or T atoms were injected into the top surface of the substrate. Injected ions are represented by the corresponding charge neutral atoms in the simulations for the sake of simplicity. Before each cycle of injection, the excess thermal energy of the system provided by the previous atomic injection is removed and the substrate is set in thermal equilibrium at 300K again. Resulting sputtering phenomena following each injection are recorded for later analysis. In our simulations, typically 5000 atoms are injected into the model substrate, which corresponds to 1.2×10^{17}/cm^2 in terms of fluence, i.e., accumulated dose, for a substrate of 2.0×2.1nm^2 in area.

Unlike earlier MD simulation studies on similar sputtering phenomena reported in Refs. 3 and 4, the simulation presented here is *accumulative*, in the sense that incident species that do not naturally leave the substrate remain in the simulation cell and therefore the substrate surface is self-consistently modified as the simulation evolves [5].

3. Simulation Results

Shown in Fig. 1 is the surface topography of the graphite substrate after 1.19 $\times10^{17}$/cm^2 fluence of H atom injections with the incident energy of 25eV (b) or 50eV (b). It is clearly seen that the substrate surface is significantly hydrogenated and the thickness of the hydrogen rich layer is about 2 nm in the case of 25eV and about 4nm in the case of 50eV. In Fig. 1 (b), among injected

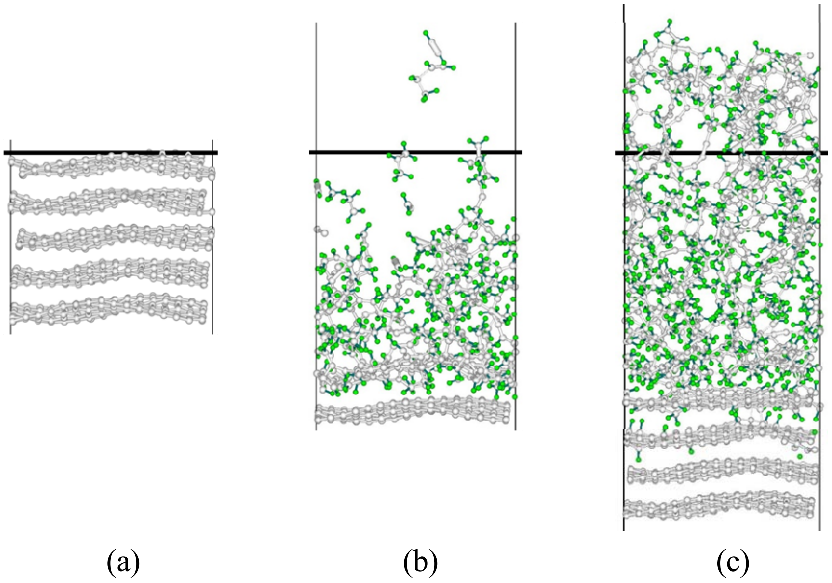
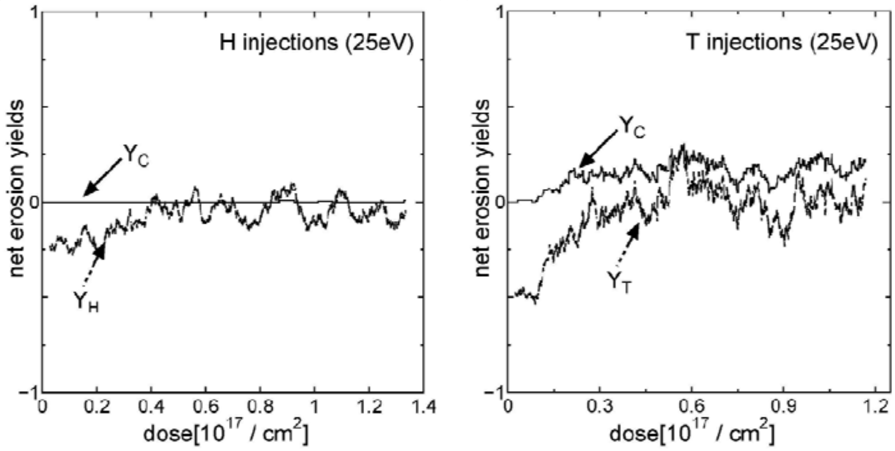

(a) (b) (c)

Fig. 2: Surface morphologies of tritium (T) injection simulations for a graphite substrate. (a) The initial substrate of 1.97 x 2.13 nm^2 in area. (b) The substrate after 1.19 x $10^{17}/cm^2$ fluence of 25eV T injections. (c) The substarate after 1.19 x $10^{17}/cm^2$ fluence of 50eV T injections. The solid horizontal lines indicate the position of the initial top surface.

5000 H atoms, 405 H atoms (8.1%) remain in the substrate whereas, in Fig. 1(c), 588 H atoms (11. 8%) remain in the substrate. The rest of injected H atoms are either reflected or desorbed from the surface. Note that, as the incident kinetic energy increases, the hydrogen rich layer tends to be formed below the top surface as fast H atoms tend to pass through the very top substrate layers without being trapped. Since we ignore various thermal processes in our MD simulations, including atomic diffusion in the substrate, hydrogen atoms in Fig. 1 may stay in the original trap sites more persistently than they should in reality.

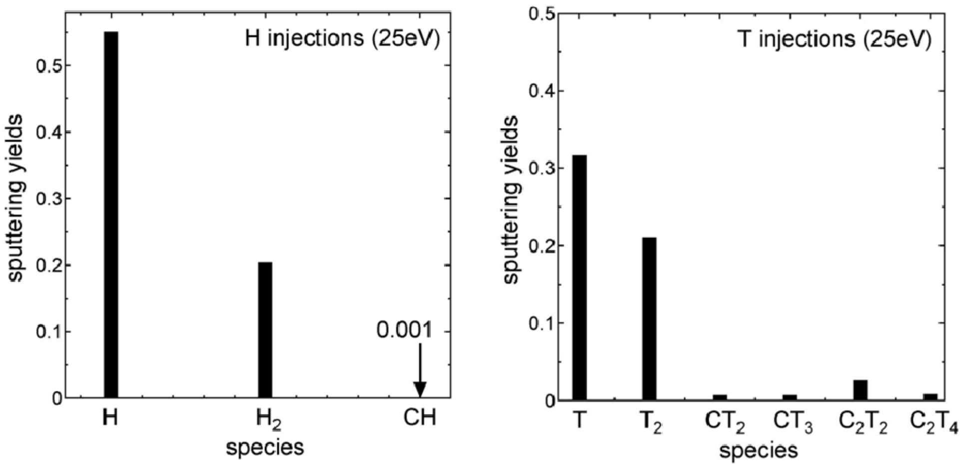
Shown in Fig. 2 is the surface topography of the graphite substrate after $1.25\times10^{17}/cm^2$ fluence of T atom injections when the incident kinetic energy is 25eV (b) or 50eV(c). As in Fig. 1(a), Fig. 2(a) shows the initial substrate. Since a T atom is three times heavier than a H atom, its incident velocity is lower than that of a H atom for a given incident energy. Therefore T atoms are more likely to be trapped near the top surface, resulting in the formation of a T rich layer closer to the top surface, as shown in Fig. 2(b) and (c). This also enhances the sputtering yield of substrate carbon atoms. The number of T atoms remaining in the substrate is similar to that in the case of H atom injections. In the figures shown in Fig. 2, 330 T atoms (6.6%) out of 5000 injected T atoms remain in the substrate at 25eV injections (b) whereas 669 (13.4%) remain in the substrate at 50eV injections.

The sputtering yield for a specific species A means the number of A atoms removed from the surface for a single injection of incident species, which we denote SY_A in this article. For species that are also used as incident species (i.e., H, D, or T in this study), however, it may be more convenient to use the "net erosion yield, " which we define as the $SY_B - I_B$, where SY_B denotes the sputtering yield of species B and I_B denotes the number of B atoms supplied by a single injection. For example, in the case of H atom injections in our simulations, we have $I_H=1$, so that we have the relation $Y_H = SY_H - 1$. If the net erosion yield is negative, the denoted species is being



(a) (b)

Fig.3: Net erosion yields Y_C, Y_H, and Y_T for C, H, and T atoms, respectively, when H atoms (a) or T atoms (b) injected into the graphite substrate at incident kinetic energy of 25eV. The incident beam is normal to the surface. The horizontal axis represents the fluence (dose) of incident atoms.



(a) (b)

Fig.4: Sputtering yields of major sputtered species in the case of 25eV injections of H (a) or T (b) atoms into the graphite substrate. Yields of H, H_2, T, and T_2 include those reflected from the surface. It is shown that C_2T_2 is the most abundant sputtered carbon-containing products at 25eV T injections.

accumulated in the substrate. In our simulations, clearly the sputtering yield and the net erosion yield for carbon have the same value as no carbon is injected during the process.

Figure 3 shows the dose (i.e., fluence) dependence of the net erosion yields evaluated as averaged values of instantaneous net erosion yields over 200 injections around the dose indicated in the figure. The cases of injecting H (a) and T (b) into the graphite surface at 25eV are given in the figure. In the case of 25eV H injections, it is seen that the graphite substrate is hardly etched and hydrogen atoms are still being accumulated up to the dose of about 1.3×10^{17} /cm^2. The carbon sputtering yield Y_C averaged over the dose from 0.82×10^{17} to 1.36×10^{17} /cm^2 given in Fig. 3(a) is 2.5×10^{-3}. On the other hand, for heavier T injections with the same kinetic energy, the graphite substrate is etched to a much larger extent and T accumulation reaches steady state, i.e., the net

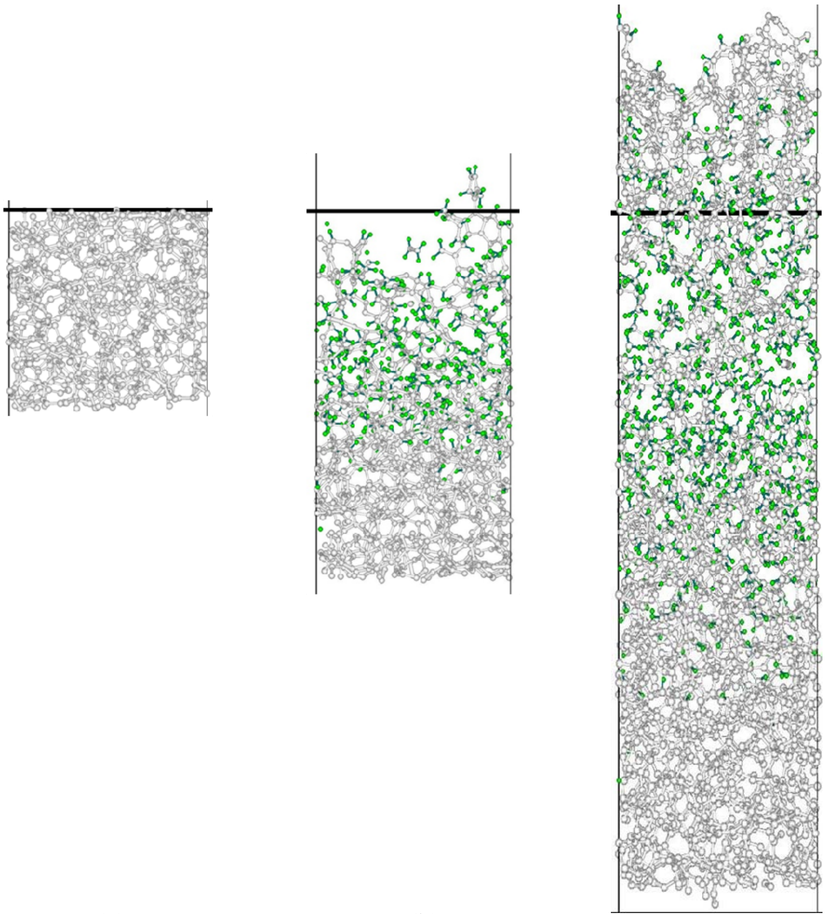
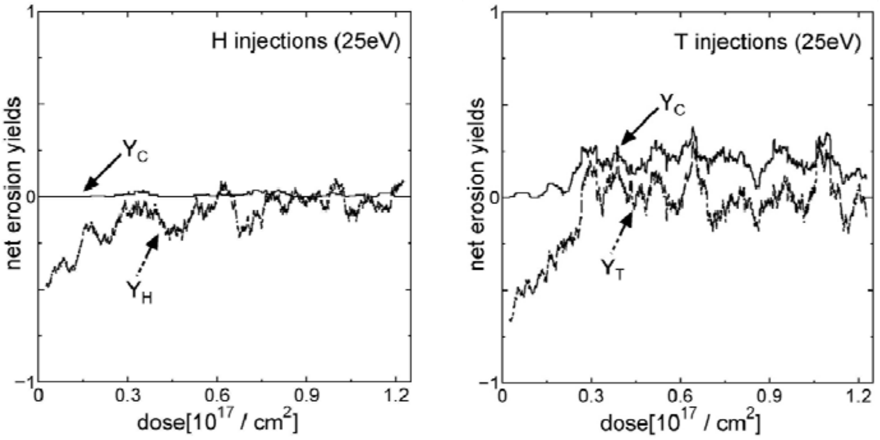


Fig.5: Surface morphologies obtained from atomic hydrogen (H) injection simulations for the amorphous substrate. (a) The initial substrate of 2.00 x 2.00 nm^2 in area.. (b) The substrate after 1.25 x 10^{17}/cm^2 fluence of 25eV H injections. (c) The substrate after 1.25 x 10^{17}/cm^2 fluence of 50eV H injections. The solid horizontal lines indicate the position of the initial top surface.

erosion yield $Y_T \approx 0$, after the sufficient number of injections. The carbon sputtering yield Y_C averaged over the dose from 0.72 x 10^{17} to 1.19 x 10^{17}/cm^2 given in Fig. 3(b) is 0.164.

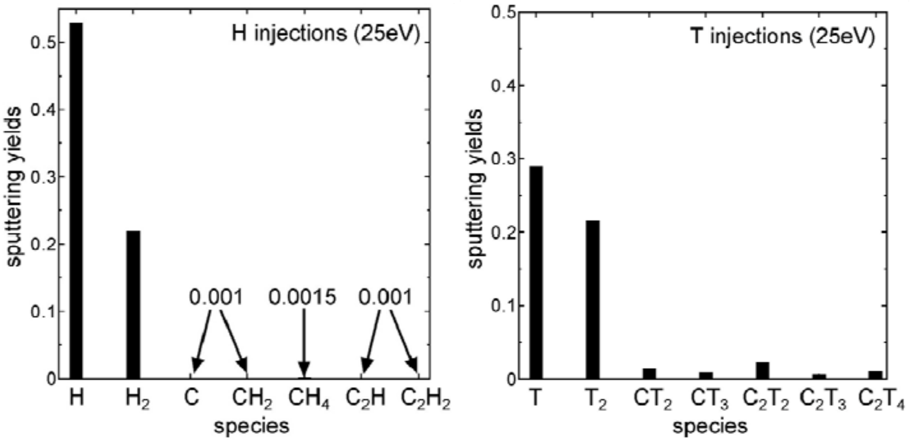
Figure 4 shows the sputtering yield of each atomic or molecular species C_xH_y (a) or C_xT_y (b) obtained from MD simulations. The yield data are averaged over 2000 injections, i.e., from 0.82 x 10^{17} to 1.36 x 10^{17}/cm^2 for (a) and from 0.72 x 10^{17} to 1.19 x 10^{17}/cm^2 for (b). The injected species is H (a) or T (b) and the kinetic energy is 25eV in both cases. The substrate is graphite. In Fig. 4(a) a very few hydrocarbon clusters are shown to be sputtered from the surface. On the other hand, in Fig. 4(b), a relatively large carbon-containing species are desorbed from the substrate surface. Indeed C_2T_2 is found to be the most abundant sputtered carbon-containing products under the conditions given here. .

The difference in the sputtering characteristics shown in Figs. 3 and 4 seems to arise from the fact that, under the same incident energy, T atoms tend to accumulate closer to the top surface and break up the carbon-carbon bonds more completely, making the substrate more amenable to sputtering under strong impact. The fact that a T atom is three times heavier than a H atom makes the momentum of the incident T atom is larger than that of the incident H atom under the same incident energy, which may also contribute to the increase of sputtering for heavier species.



(a) (b)

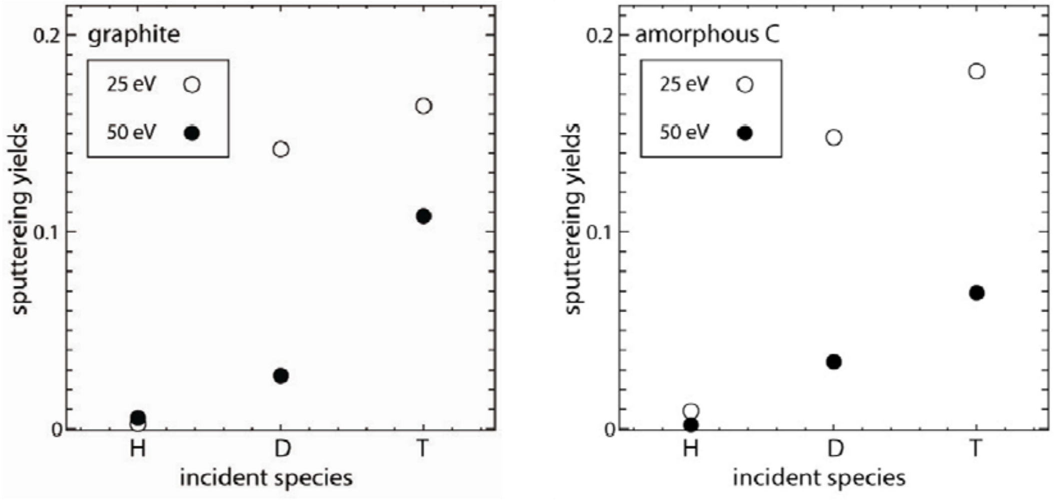
Fig.6: Net erosion yields Y_C, Y_H, and Y_T for C, H, and T atoms, respectively, when H atoms (a) or T atoms (b) injected into the amorphous substrate at incident kinetic energy of 25eV. The incident beam is normal to the surface. The horizontal axis represents the fluence (dose) of incident atoms.



(a) (b)

Fig.7: Sputtering yields of major sputtered species in the case of 25eV injections of H (a) or T (b) atoms into the amorphous substrate. Yields of H, H_2, T, and T_2 include those reflected from the surface. It is shown that C_2T_2 is the most abundant sputtered carbon-containing products at 25eV T injections.

We now examine similar effects for different substrates. Figure 5 shows the surface topographies of the amorphous carbon substrate in the initial state (a), after $1.25 \times 10^{17}/\text{cm}^2$ fluence of H atom injections at 25eV (b) and $1.25 \times 10^{17}/\text{cm}^2$ fluence of H atom injections at 50eV (c). As in Fig. 1, it is clearly seen that the substrate surface is significantly hydrogenated and thick hydrogen rich layers are formed. In the case of Fig. 5(b), among 5000 injected H atoms, 550 H atoms (11.0%) remain in the substrate whereas, in the case of Fig. 5(c), among 5000 injected H atoms, 843 H atoms (16.7%) remain in the substrate. When heavier hydrogen isotopes, i.e., D or T, are injected, on the other hand, such isotope species tend to be trapped closer to the top surface, similar to the case of Fig. 2.



(a) (b)

Fig. 8: Isotopic effects of sputtering yields for injection energies of 25eV (open circles) and 50 eV (closed circles), obtained from MD simulations. The vertical axis represents the number of C atoms removed from the surface per injection of H, D, or T atom. The substrates used for the simulations are (a) graphite and (b) amorphous carbon.

Figure 6 shows the dose (i.e., fluence) dependence of the net erosion yields when H (a) or T (b) atoms are injected into the amorphous substrate at 25eV. The carbon sputtering yield Y_C averaged over the dose from 0.75 x 10^{17} to 1.25 x 10^{17}/cm^2 given in Fig. 6(a) is 9.0 x 10^{-3}. On the other hand, for heavier T injections with the same kinetic energy, the amorphous substrate is clearly etched and T accumulation reaches steady state, i.e., the net erosion yield $Y_T \approx 0$, after the sufficient number of injections, as in the case of the graphite substrate given in Fig. 3. The carbon sputtering yield Y_C averaged over the dose from 0.75 x 10^{17} to 1.25 x 10^{17}/cm^2 given in Fig. 6(b) is 0.182.

Figure 7 shows the sputtering yield of each atomic or molecular species C_xH_y (a) or C_xT_y (b) when the amorphous carbon substrate is subject to H (a) or T (b) bombardment at 25eV kinetic energy. The yields are averaged over the dose from 0.75 x 10^{17} to 1.25 x 10^{17}/cm^2 (i.e., over 2000 injections in MD simulations). As in the case of Fig. 4, a very few hydrocarbon clusters are shown to be sputtered from the amorphous surface when it is subject to 25eV H injections. On the other hand, in the case of 25eV T injections, a relatively large carbon-containing species are desorbed from the substrate surface and, as in the case of the graphite substrate, C_2T_2 is found to be the most abundant sputtered carbon-containing products under the conditions given here.

Figure 8 summaries the dependence of the total C sputtering yield (i.e., the total number of C atoms removed from the surface per injection) on the mass of the injected hydrogen isotopes. The yields shown here are the averaged yields when the systems are considered to be in steady state, as in the cases shown in Fig. 4 and 7. The model substrate used for the simulations given here are the graphite (a) and amorphous carbon (b). It is seen that, while H atoms hardly etch either graphite or amorphous carbon substrates at energies lower than 50eV examined here, there is strong dependence of the C sputtering yield on the energy for heavier isotopes. Isotope effects of the sputtering is also clearly shown in Fig. 8

4. Discussion and Conclusions

MD simulation for plasma surface interactions for graphite and amorphous carbon substrates have shown that accumulation of D or T near the top surface significantly increases the total carbon sputtering yields especially at low incident energies. The significant increase of D or T sputtering yields have been observed at accumulation dose over $10^{16}/\mathrm{cm}^2$ in the simulations. Isotopic effects of sputtering yields have also been observed. The large difference between H and D sputtering yields observed in our simulations is qualitatively consistent with experimental observations given in Ref. [7]. Breakup of substrate bonds by accumulated D or T near the top surface is considered to account for the strong isotropic effects as well as relatively larger sputtering products observed in the cases of D or T injections.

Acknowledgements

The authors thank Dr. H. Yamada for his useful discussion and helpful support for numerical simulations in this work.

References

[1]H. Yamada and S. Hamaguchi, J. Appl. Phys. **96**, 6147 (2004).
[2]M. Yamashiro, H. Yamada, and S. Hamaguchi, J. Appl. Phys. **101** 046108 (2007).
[3]E. Salonen, K. Nordlund, J. Keinonen, and C. H. Wu, Phys. Rev. B **63**, 195415 (2001).
[4]J. Marian, L. A. Zepeda-Ruiz, N. Couto, E. M. Bringa, and G. H. Gilmer, J. Appl. Phys. **101,** 044506 (2007).
[5]P.S. Krstic, C.O. Reinhold, and S.J. Stuart, New J. Phys. **9**, 209 (2007).
[6]D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).
[7]J. Roth and J. Bohdansky, Nucl. Instrum. Mech. B **23** 549 (1987).