

## Molecular Dynamics Study of Plasma Surface Interaction of Codeposited Materials

K. Ohya 1), K. Inai 1), N. Mohara 1), Y. Miyake 1), A. Kirschner 2), D. Borodin 2), R. Doerner 3), Y. Ueda 4), T. Tanabe 5)

1) The University of Tokushima, Tokushima 770-8506, Japan

2) Forschungszentrum Jülich, D-52425 Jülich, Germany

3) University of California at San Diego, La Jolla, CA 92093, USA

4) Osaka University, Osaka 565-0871, Japan

5) Kyushu University, Fukuoka 812-8581, Japan

E-mail contact of main author: ohya@ee.tokushima-u.ac.jp

**Abstract.** Material mixing has attracted great interest since ITER has beryllium (Be), carbon (C), and tungsten (W) as the plasma facing components. It drastically changes plasma surface interactions of the underlying substrate materials. A molecular dynamics simulation code was developed for analyzing sputtering characteristics of ITER mixed materials and was applied to investigate subsequent effects of introducing Be impurities to codeposited C layers. Amorphous C (a-C) layers containing hydrogen (H) with atomic ratios of  $H/(C+H) < 0.3$  together with Be deposition with the percent coverage of up to 92% are produced on top of a tungsten (W). Noncumulative bombardment of the a-C layer without H (i.e.  $H/(C+H)=0$ ) by H atoms with energies of 1–100 eV, is subject to only C physical sputtering. The H uptake in the a-C deposition layer enhances C sputtering owing to the formation of the loosely-bound C chains, producing the sputtering even at energies much less than the threshold energy for physical mechanism, in addition to chemical  $CH_y$  sputtering. Concerning  $CH_y$  sputtering in the eV energy range, larger radicals are emitted with increasing surface temperature. The Be, deposited on the a-C:H layer, clearly reduces both C and  $CH_y$  sputtering due to the formation of Be-C and Be-H bonds in the vicinity of the surface. The reduction rate is enhanced due to an increase of surface temperature and a decrease of H impact energy. Such mechanisms reproduce recent finding of strong mitigation of chemical erosion of a C target exposed to a Be-seeded plasma in PISCES-B experiments.

### 1. Introduction

The initial material selection for the ITER divertor was carbon fiber composite (CFC) around the strike points on the inner and outer divertor targets and tungsten (W) on the upper baffle and dome. Since CFC is subject to strong chemical sputtering due to the bombardment with high-flux hydrogen (H) isotopes. Eroded carbon (C) and hydrocarbons ( $CH_y$ ,  $C_2H_y$ , ...) migrate and redeposit on other locations, forming hydrogen-rich codeposition (a-C:H) layers on CFC, while a formation of W-C mixed layers will appear on W. Furthermore, beryllium (Be) used for most parts of the first wall of ITER is subject to strong physical sputtering due to its low surface binding energy in comparison with C and W. Since a portion of eroded Be atoms migrates towards the divertor regions, a Be deposition and mix layer formation of Be-C and Be-W will appear on the divertor components as well.

We have developed a molecular dynamics (MD) simulation code that treats the interaction of fuel H and plasma impurities (C,  $C_xH_y$ , Be and W) with such mixed materials for ITER [1-4]. In the MD code, the Brenner potentials for covalent bonds are used for the C-C and C-H interactions [5], and for other interactions, parameter-described families of analytical bond-order potentials are taken from Juslin et al. [6] and Björkas et al. [7,8].

Concerning chemical sputtering of a-C:H layers, a better understanding is required of the origins of the composition of released hydrocarbons and its change with ion energy and surface temperature, as well as of the flux dependence of erosion yields observed in fusion experiments [9]. The effect of Be impurities has recently demonstrated in experiments at

plasma divertor simulator PISCES-B [10,11]. The method of seeding Be onto a plasma, in contact with a C target, was shown to decrease the chemical erosion rate to negligible levels, even at a small Be concentration  $\sim 0.1\%$  in the plasma. Dedicated studies are continuing to understand the mitigation mechanisms, depending on ion energy, Be concentration and surface temperature [12], and this includes an analysis of the transport of the eroded impurities in the plasma [13]. Therefore, the present work is devoted to studying the effect of Be impurities to chemical sputtering in the energy range of  $<100$  eV, which approximates the threshold energy of physical sputtering. This paper has primarily focused on the Be deposition effect to C chemical erosion, although relevant work using a-C:H layers has been performed.

## 2. Preparation of a-C and a-C:H layers and introducing Be impurities

An amorphous C (a-C) layer is prepared by the bombardment of a small crystal W bcc cell consisting 4000 atoms by 10 eV C atoms [1]. In a classical MD scheme, the atomic trajectories are followed, up to 1 ps with a time step of 0.05 fs. From cumulative impacts of 5000 C atoms, an a-C layer with a thickness of more than 2 nm is formed on the W. The H uptake in the a-C layer is performed by simultaneous bombardment with C and H atoms with a total number of 2000. The H impact energy (1–30 eV) is changed to control the atomic ratio

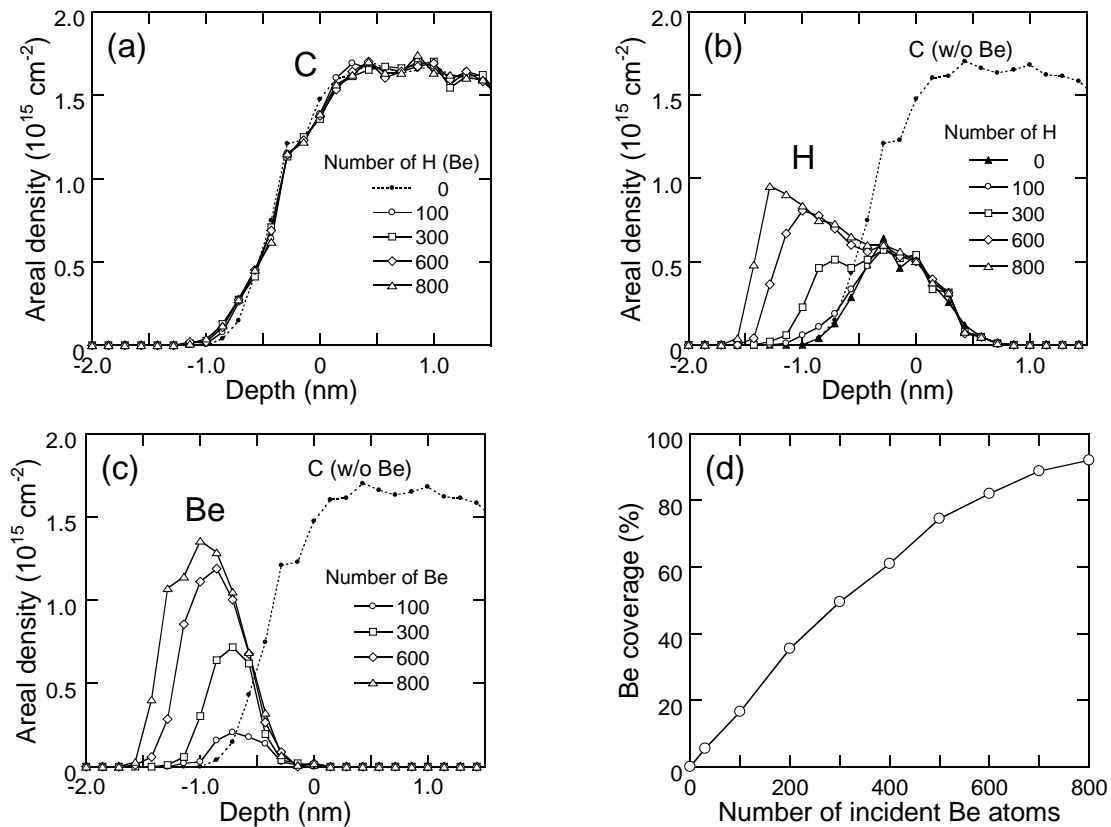


FIG. 1. Depth profiles of (a) C, (b) H and (c) Be in an a-C:H layer bombarded at different number of Be and H atoms. (d) Relationship between the number of bombarding Be atoms and the percent coverage of the Be deposition. An a-C:H layer with the averaged  $H/(C+H)$  ratio of 0.3 is simultaneously bombarded by H and Be atoms. The positive (negative) depths correspond to net erosion (deposition).

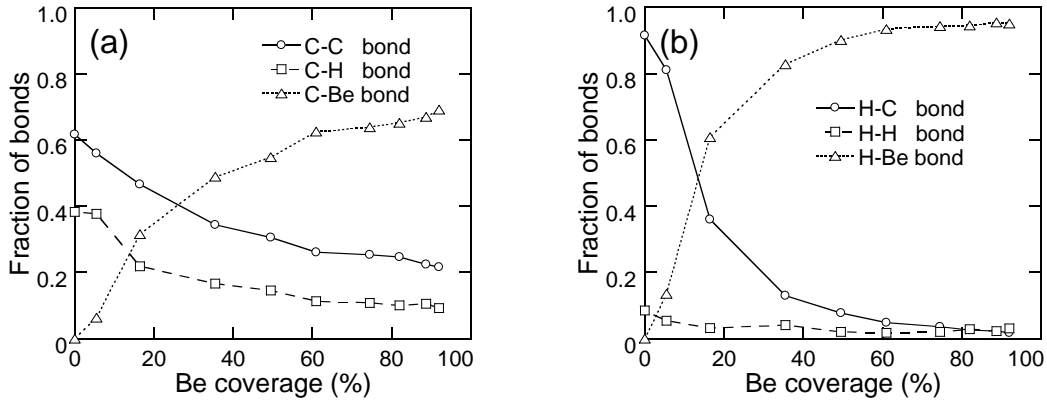


FIG. 2. Fraction of different bonds with (a) C atoms and (b) H atoms in a depth above  $-0.47$  nm, as a function of the percent coverage of Be deposition on an a-C:H layer.

of  $H/(C+H)$  in the layer, whereas the C energy is kept to be 0.025 eV. The maximum  $H/(C+H)$  ratio is approximately 0.30 on average over a  $-0.43$  nm to  $0.14$  nm depth for the bombardment of 1 eV H. The C and H depth profiles in the layer are shown in Figs. 1(a) and 1(b) (no injection of Be (H)). Here, the initial surface of the a-C before the H uptake is approximately zero-depth. The positive and negative depths correspond to the net erosion and net deposition, respectively. Be atoms are deposited on the a-C:H layer by simultaneous bombardment with 10 eV Be and 1 eV H atoms. The Be deposition on the layer increases with increasing number of incident Be atoms (Fig. 1(c)), where incident H atoms are codeposited as well (Fig. 1(b)). The percent coverage of the Be deposition by one or more atomic layers is increased with increasing number of incidence, up to 92 % for the incidence of 800 Be atoms, as shown in Fig. 1(d).

Figures 2(a) and 2(b) show the fractions of different bonds with C and H atoms, respectively, in the top surface at a depth above  $-0.47$  nm. The fraction of C-Be and H-Be bonds increases steeply with increasing Be coverage, whereas the fraction of C-H and C-C bonds decreases.

### 3. Interaction of low-energy H atoms with codeposited layers

Noncumulative bombardments of the above-prepared surfaces with 1000 H atoms of differing energies of 1–100 eV are performed and the same initial surface is used for each simulation. The incident atoms hit the top surface at random positions. The target temperature is controlled to be 300, 800 and 1200 K by using Langevin thermostat [14] with a time constant of 10 fs every time steps. This procedure dissipates the excess heat resulting from a small cell used here. Atoms and molecules, which pass through a virtual surface at a distance of  $-2.0$  nm apart above the initial surface (see Fig. 1), are counted as sputtered particles, so that the distribution of the sputtered species (C,  $C_xH_y$ , and Be) is determined by repetitive impacts. Figures 3(a) and 3(b) show the probabilities of finding a projectile H atom at a depth every 1 fs in and out the target material. The distribution indicates that the dominant interactions of H atoms occur within the top surface of the a-C:H layer with a thickness of 1–2 nm. Furthermore, it should be noted that the interaction layer tends to move from the a-C:H layer to Be deposition layer with increasing Be coverage and decreasing H impact energy.

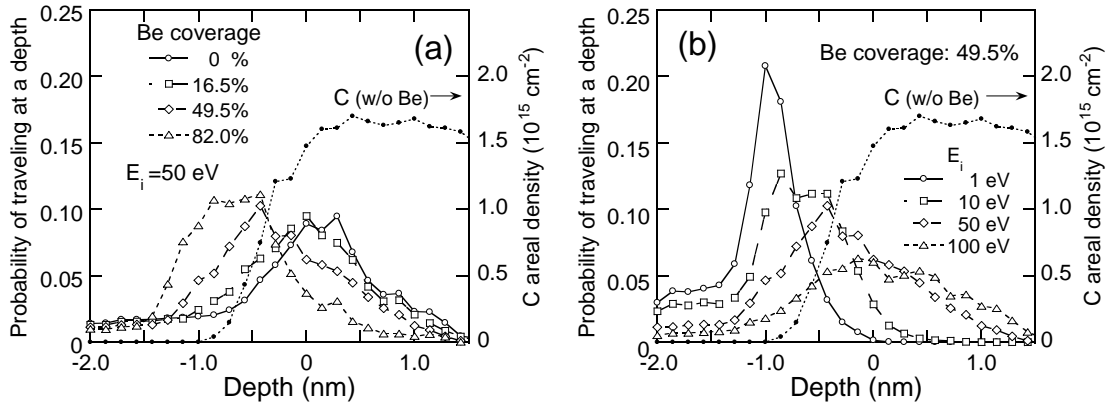


FIG. 3. Probability distribution that a projectile H atom travels at a depth of an a-C:H layer at (a) different percent coverage by Be with the impact energy of 50 eV and (b) different H impact energy with the Be coverage of 49.5%.

#### 4. Energy- and temperature-dependent sputtering of codeposited layers

If there is no uptake of H in an a-C layer,  $\text{CH}_y$  emission is very rare and the energy dependence of the sputtering yield for C atoms indicates a clear threshold for physical sputtering at an impact energy (e.g., 38.1 eV [15]), as shown in Fig. 4(d). By H uptake in the a-C layer, chemical sputtering occurs and various radicals are emitted even at the target temperature of 300 K (Fig. 4(a)). This is caused by loosely bonding of C-C system due to the uptake of H in the a-C. With increasing target temperature, chemical sputtering from the a-C:H layer is clearly enhanced. At the temperature of 800 K (Fig. 4(b)), a maximum value of sputtering yield is observed in the energy range of eV, where heavier hydrocarbons are more emitted with decreasing H impact energy. Small amounts of  $\text{C}_2$  and ethane and propane families are also emitted. Furthermore, the H uptake produces sputtering of loosely-bound C at energies much less than the threshold energy for physical sputtering, giving large sputtering yields at low energies [16].

#### 5. Chemical erosion mitigation of codeposited layers due to Be deposition

As shown in Fig. 5, C and  $\text{CH}_y$  sputtering are clearly suppressed by introducing Be deposition on the layers, whereas additional Be sputtering appears. With increasing target temperature, Be atoms are more sputtered and a small part of molecules including Be, C and H is emitted. Furthermore, the Be sputtering occurs even at energies of less than the threshold energy for physical sputtering (15.3 eV, [15]). Such low-energy (<10 eV) sputtering of Be was verified very recently by an MD calculation for Be due to the bombardment with deuterium atoms, and also by experiments [17]. This correspondence is resulted from due to the formation of H-Be bonds in the vicinity of the surface, as shown in Fig. 2(b), together with an increasing deposition of Be.

In Fig. 6, C and  $\text{CH}_y$  sputtering yields normalized at the yield for an a-C:H layer without Be deposition are shown as a function of the percent coverage of Be deposition at different H impact energies. The decrease in C and  $\text{CH}_y$  sputtering yields is much faster than an increase of Be coverage for both. The C sputtering yield is strongly reduced by a small deposition (<10%) of Be on the a-C:H layer. However, for high impact energies (50 and 100 eV) there still remains even at the Be coverage of more than 50%, due to physical sputtering

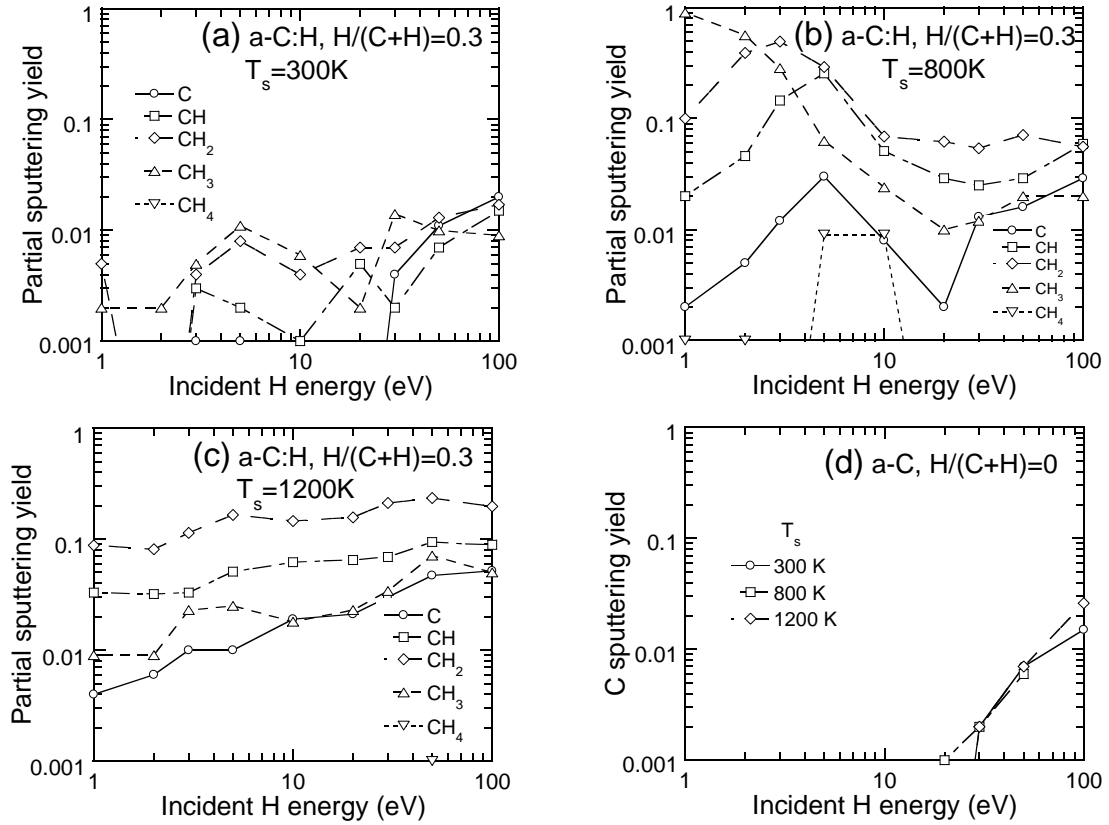


FIG. 4. Energy dependence of partial C and  $\text{CH}_y$  sputtering yield of a-C:H layers (a, b and c) and an a-C layer (d) with target temperatures of 300 K, 800 K and 1200 K.

mechanism as demonstrated by a Monte Carlo calculation [18]. The reduction of  $\text{CH}_y$  sputtering yields shows a good correspondence with mitigation of chemical erosion (i.e., the decrease in CD band light emission) of a C target exposed to a Be-seeded plasma in PISCES-B experiments [11], as plotted in Figs. 6(c) and 6(d). The calculated changes are somewhat slower than that for C sputtering. It is clearly seen that the reduction rate increases with increasing target temperature and decreasing H impact energy. Since the Be surface coverage increases with exposure time of plasma containing a small amount ( $<1\%$ ) of Be impurity before its saturation, our simulation can explain the surface temperature ( $T_s$ ) and ion energy ( $E_i$ ) dependence of decay time,  $\tau_{\text{Be/C}}$ , of chemical CD light emission observed in PISCES-B [12].

The reason for the reduction of C and  $\text{CH}_y$  sputtering can be explained within our simulation model by stronger bonding of Be-C system than for C-H and C-C bonds, leading to a formation of Be-C compound on the surface, as demonstrated in [10]. The Be-C system has a longer attractive interaction range (the dimmer bond distance,  $r_0 = 1.72 \text{ \AA}$ , and the center of the cut-off distances,  $R = 2.60 \text{ \AA}$ ) than that for the C-H system ( $r_0 = 1.12 \text{ \AA}$  and  $R = 1.55 \text{ \AA}$ ) and C-C system ( $r_0 = 1.39 \text{ \AA}$  and  $R = 1.85 \text{ \AA}$ ) [7]. This results in the formation of Be-C bonds in the vicinity of the surface so that C-H bonding (and subsequently,  $\text{CH}_y$  sputtering) is suppressed. As shown in Figs. 3, the shift of dominant interaction layer from the a-C:H layer to a Be deposition layer suppress a production of C-H bonding with increasing Be coverage and decreasing ion energy, where projectile H atoms are bound mostly with Be atoms (Fig. 2).

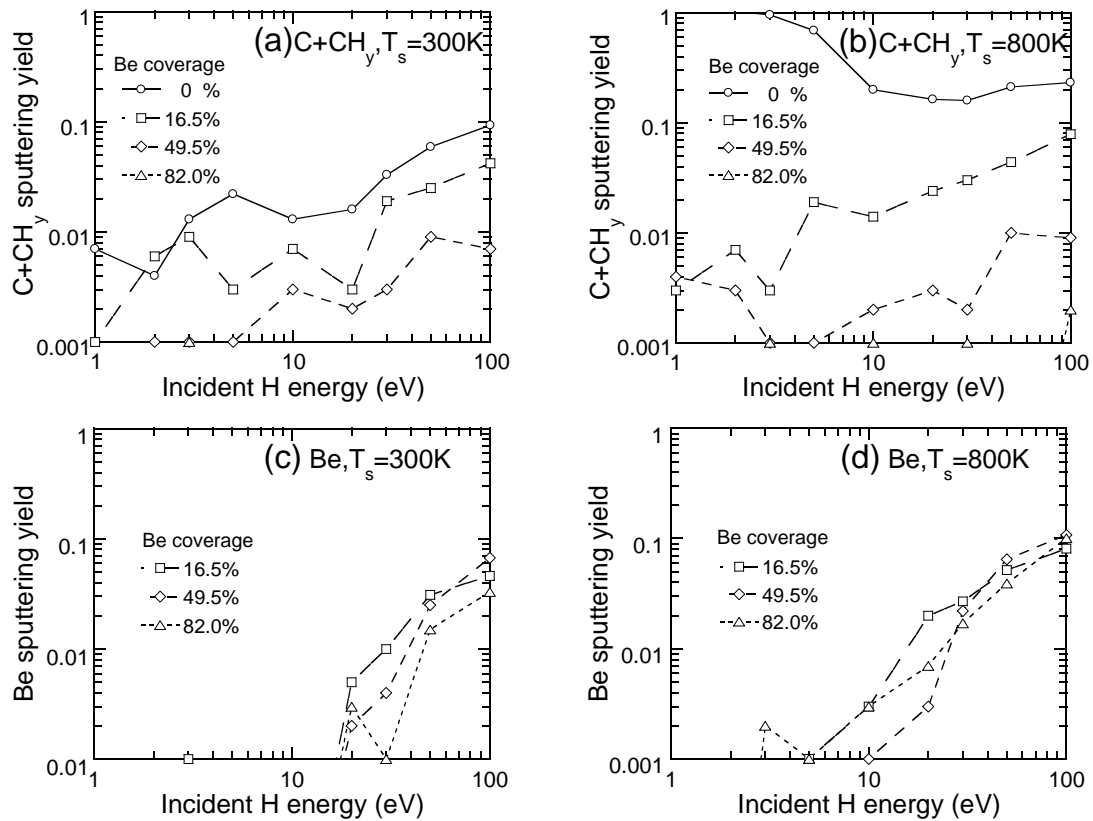


FIG. 5. Energy dependence of total ( $C+CH_y$ ) sputtering yield (a and b) and Be sputtering yield (c and d) of  $a$ -C:H layers deposited by Be impurity at different percentage of coverage. The target temperatures are 300 K (a and c) and 800 K (b and d).

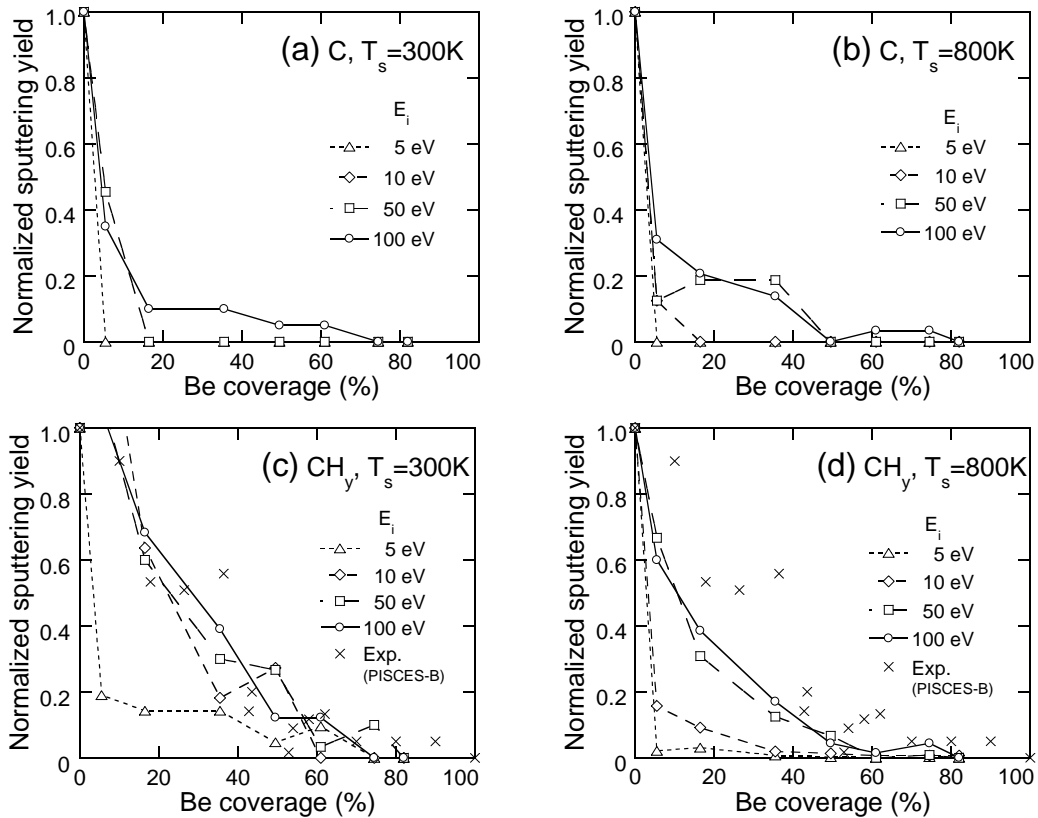


FIG. 6. Normalized C and  $CH_y$  sputtering yield of an  $a$ -C:H layer as a function of the percent coverage of Be deposition at different H impact energies.

## 6. Concluding remarks

The interaction of low-energy (1–100 eV) hydrogen (H) atoms with hydrogen-rich co-deposited C (a-C:H) containing Be impurity is investigated by means of molecular dynamics (MD). Amorphous C (a-C) layers without H uptake is subject to only C physical sputtering, whereas the H uptake causes C sputtering at energies much less than the threshold energy for physical mechanism, in addition to chemical CH<sub>y</sub> sputtering. The Be, deposited on the a-C:H layer, clearly reduces both C and CH<sub>y</sub> sputtering due to the formation of Be-C and Be-H bonds in the vicinity of the surface. Such mechanisms reproduce recent finding of strong mitigation of chemical erosion of a C target exposed to a Be-seeded plasma in PISCES-B experiments. The results on the sputtering characteristics, which depend on the concentration of the hydrogen and the impurities in the co-deposition, are necessary to evaluate and control the tritium inventory of the plasma facing walls in ITER.

## Acknowledgement

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