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Enhanced erosion of tungsten by atom clusters

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Abstract

Self-sputtering of tungsten, a plasma-facing material candidate in fusion devices, by ionized atoms is a widely studied phenomenon. However, not only single atoms, but also small clusters sputtered from plasma-facing surfaces can be ionized in the sheath and redeposited back on the first wall. Using molecular dynamics simulations we study the self-sputtering of tungsten by small W_n ($n = 1, 2, 4$) clusters in the energy range 0.2–40 keV/cluster. We show that, in comparison with single-atom sputtering yields, enhanced sputtering yields by clusters are observed at energies higher than about 2 keV/atom. The yields are proportional to the number of atoms in the cluster at 40 keV/cluster. However, cluster bombardment at energies lower than 2 keV/cluster is not self-sustaining and will reduce to single-atom redeposition.

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1. Introduction

Tungsten is one of the candidates for plasma-facing component (PFC) materials in fusion devices due to its high melting point, thermal conductivity and long operation lifetime under bombardment by helium and hydrogen isotopes [1–3]. Especially important characteristics of tungsten are the lack of chemical sputtering by low-energy hydrogen atoms and ions and low hydrogen retention [4] in comparison with, e.g. graphite. However, one issue with the suitability of tungsten as a PFC material is self-sputtering. Species sputtered from tungsten surfaces obtain a charge state due to collisions with the electrons in the plasma. This leads to redeposition as the ionized species are accelerated by the sheath potential [5,6]. The self-sputtering yields of tungsten are usually orders of magnitude higher than for hydrogen bombardment [7]. If the self-sputtering yield is higher than one, bombardment by sputtered species alone can erode the material away (runaway sputtering).

Although tungsten exhibits a quite high ionization rate coefficient for electron impact [8] compared with e.g. Be and C, some of the sputtered species do not redeposit but instead penetrate the core plasma. This leads to radiative cooling of the plasma proportional to values from Z^2 to Z^4, where Z is the atomic number of the impurity atoms. Hence, tungsten atoms are extremely harmful plasma impurity species for fusion device operation. With increasing self-sputtering the concentration of impurities in the core plasma can be expected to increase as well.

The impact energy distribution of the redeposited species, and hence the overall erosion yield, depends on the electron temperature T_e of the sheath and the charge state of the impinging species. According to calculations by Brooks et al. [5,6], for $T_e = 30$ eV the mean charge state of redeposited W ions is about 2–3, resulting in average impact energies between 200 and 500 eV. Higher charge states and redeposition energies are observed for higher T_e. It is therefore necessary to know the energy and angular dependence of W self-sputtering to determine the limit of acceptable T_e.

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Although tungsten sputtering by single atoms (i.e. monomers) has been extensively studied experimentally [9–12] as well as with calculations based on the binary collision approximation (BCA) [5–7], much attention has not been given to sputtering induced by atom clusters. Yet atom clusters can be produced both by ion impacts [13,14], arcing [15] and blistering [16,17], which may all occur in fusion devices. Moreover, the sputtering due to clusters has recently been shown in some cases to be dramatically larger than the sputtering yield for ionized atoms. Andersen et al. [18] find that the self-sputtering yield Y_n for an Au cluster of n atoms is

$$Y_n(E_{\mathrm{tot}}) \sim n^2 Y_1(E_{\mathrm{tot}}), \tag{1}$$

where Y_1 is the sputtering yield by single atoms, for the same total kinetic energy E_{tot} of the cluster in the energy range 40–10 000 keV/cluster. On the other hand, molecular dynamics (MD) simulations of Au(1 1 1) sputtering by 16-keV Au clusters by Colla et al. [19] give sputtering yields proportional only to the first power of the number atoms in the clusters. An analytical explanation for these effects is not available, but it seems that the transition to the quadratic enhancement of sputtering (Eq. (1)) commences through a transitional energy regime ($Y_n \sim n$) seen in the MD simulations.

It is not clear whether the sputtering yield enhancement by clusters [18,19] applies directly to the case of low-energy self-sputtering of W in fusion reactors. First, the bcc metal W has much higher hardness and melting point than the fcc metal Au. Second, the energies of interest in the reactors (a few hundred eV) are below the energy range where true heat spike behaviour is generally believed to be significant. However, it should be kept in mind that the redeposition energy distributions [5,6] are quite broad and impacts in the keV energy range can also be expected. Also, large chunks eroded by arcing [15] or blistering [16,17] may fragmentate upon ionization to several smaller clusters. Hence there is a real possibility that eroded atom clusters which are redeposited on a fusion device first wall could produce much more sputtering than models accounting only for single-atom sputtering can predict.

We employ MD simulations, which have been found to describe well surface effects during ion irradiation [20], to examine here whether the non-linear enhancement in sputtering from clusters is present at the energies of relevance for fusion reactors. We also evaluate what fraction of the sputtered atoms are in clusters (and hence could lead to additional cluster-enhancement in the sputtering). Tungsten monomers, dimers and tetramers are used as the irradiation projectiles, as small clusters can be expected to be the most abundant sputtered and, consequently, redeposited species.

2. Simulation principles

For the modeling of W surfaces and clusters we employed the modification of the Finnis–Sinclair potential [21] due to Ackland and Thetford [22], which we have augmented by a repulsive potential to describe well high-energy collisions [23]. We have previously shown that the potential reproduces well surface irradiation effects by comparing damage production simulations with field-ion microscopy experiments [20,23–26].

We used W(0 0 1) surfaces as the irradiation target. The surface was created by first relaxing a perfect W lattice, with periodic boundaries in all directions, at a selected temperature using the pressure and temperature scaling methods of Berendsen et al. [27]. The periodic boundaries were then removed in one direction and atoms within 0.5 nm from the opposite side of the simulation cell were held fixed. The surface was then allowed to relax for a few picoseconds. A sample temperature of 300 K was used.

We used total cluster energies in the range $E_{\mathrm{tot}} = 0.2$–40 keV. The target lattice consisted of 10 000–800 000 atoms, depending on the cluster energy. The sputtering simulations were carried out by creating a small W_n cluster ($n = 1$, 2, 4; with an optimized geometry in the last case) in a random position above the surface. In the case of the dimer or tetramer bombardments the cluster was rotated with random Euler angles to obtain an arbitrary orientation. The projectile was then assigned a velocity, corresponding to a selected kinetic energy. The direction of the cluster (center-of-mass) velocity was defined by an off-normal impact angle θ and a twist angle in the surface plane, in reference to the [1 0 0] direction.

In the present study we only consider the cases $\theta = 0°$ and 20°. For low energies ($E_{\mathrm{tot}} \leqslant 4$ keV) a random twist angle between 0° and 45° was used. However, in order to minimize channeling we used only a twist angle of 15° for the high impact energies, as determined with the `MDRANGE` computer code [28]. Since the sputtering yields are roughly proportional to the nuclear energy deposited close to the surface, the high-energy simulations can be assumed to give the highest yield estimates. Electronic stopping, as calculated by the SRIM-98 computer code [29], was included in the equations of motion of all atoms having a kinetic energy higher than 10 eV.

Depending on the projectile energy, the impact simulations were run for 10–40 ps. At the beginning of the simulation run the impact cascade was allowed to proceed freely in the lattice, aside from a temperature scaling to the original temperature within about 0.5 nm from the cell borders. The scaling at the cell borders was done to avoid artificial effects across the cell boundaries. We checked that no recoiling atoms entered the border region. After the cascade had thermalized sufficiently

(5–20 ps), the entire cell was cooled to 300 K (in ~10 ps). Each impact simulation was treated independently of the other. For reliable statistics, hundreds of impact runs were done at the lower ($\leqslant 2$ keV) energies, and 9–18 runs at the higher energies.

Particles more than 1 nm above the original surface at the end of the simulation run were counted as sputtered particles. The compositions of sputtered species (i.e. the number of atoms in sputtered clusters) were obtained from a detailed analysis of the positions of the sputtered atoms at the end of the simulation run. Test simulations of up to 100 ns with small clusters, which constitute the majority of the sputtered species, showed that the W_2 and W_3 clusters remain stable, while some of the W_4 fragmentate within 10 ns. However, along with the cluster fragmentation due to the internal temperature, an important issue to consider is possible interactions between plasma electrons and the eroded atom clusters. Treatment of this issue would require modelling of the fusion plasma and time-dependent quantum mechanical simulation of collisions between electrons and the atom clusters, which is beyond the scope of this study. Thus, as we cannot predict the stability of the clusters in the plasma, we only determine here the distributions of the clusters leaving the surface.

The sputtering yield in our modeling is taken as the average number of reflected projectile atoms plus the number atoms ejected from the lattice for a single projectile impact. Although the atomistic nature of our simulations would allow it, we do not make any distinction between reflected impact atoms and atoms ejected from the surface. As the impact projectiles are of the same atom types as the lattice atoms, this distinction serves no purpose when determining whether the irradiation produces net growth or erosion of the sample.

To ensure that our method produces realistic self-sputtering yields of tungsten, we first carried out a series of test simulations for single-atom irradiations. We chose ion energies of 350 eV and 1 keV and the normal angle of incidence. The sputtering yields for the two cases were 0.28 ± 0.02 (350 eV) and 1.32 ± 0.08 (1 keV), in comparison with the experimental yields of 0.30 [11] and 1.03 [10], respectively. The agreement between the two cases is reasonable, although it should be noted that the comparison is not quite direct. In our case the target is a single-crystalline W(0 0 1) surface while polycrystalline samples are used in the experiments. The results of this test were, however, sufficiently convincing to proceed on to the cluster bombardment simulations.

3. Results

The self-sputtering yields per cluster atom for total cluster energies between 200 and 500 eV are shown in Fig. 1. It is seen that at all energies, the yields by single atoms are much higher than those for dimers or tetramers. This is explained by the lower energies per cluster atom for increasing cluster sizes. Furthermore, at 200 eV/cluster no sputtering was observed for W_4 bombardment at $\theta = 0°$. The energy per atom in that case is below the self-sputtering energy threshold at normal incidence, about 70 eV [9].

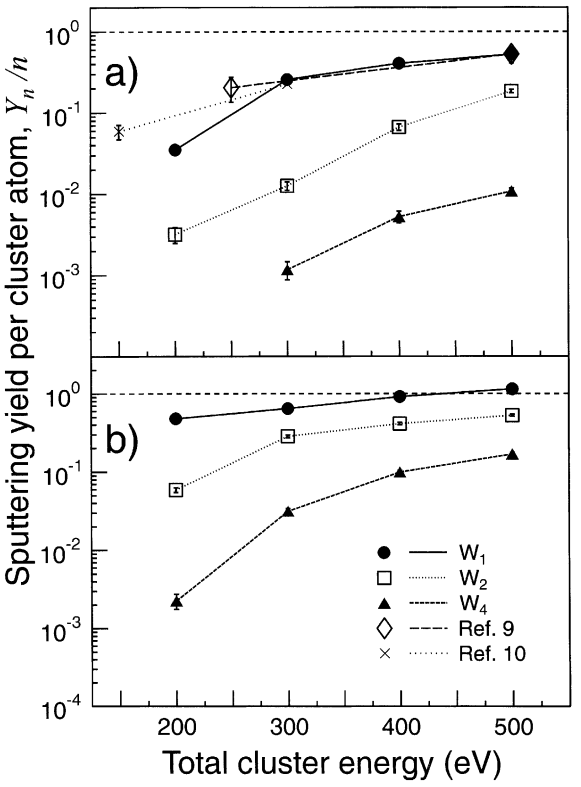

Fig. 1. Self-sputtering yields for the W_1, W_2 and W_4 bombardments, as a function of the total cluster energy E_{tot}. The off-normal angle was (a) 0° and (b) 20°. Experimental data points for self-sputtering of polycrystalline W by single atoms are also shown. The runaway sputtering limit ($Y_n/n = 1$) is shown by the dashed line.

It is well known that the threshold energy and sputtering yield of ion irradiation depend on the impact angle. For increasing impact angle the sputtering yields by the W_2 and W_4 bombardments increase more strongly than for the monomer bombardment, although they still remain well below the runaway sputtering limit. Indeed, runaway sputtering is observed only for the monomer bombardment ($\theta = 20°$) at energies above roughly 450 eV.

For low-energy irradiation the sputtering yields, for fixed energies per cluster atom $\epsilon = E_{tot}/n$, are linearly proportional to the number of atoms in the cluster

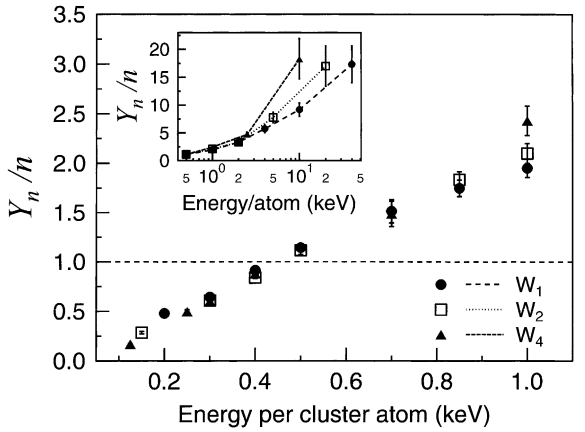

Fig. 2. Self-sputtering yields for the W_1, W_2 and W_4 bombardments ($\theta = 20°$), as a function of energy per cluster atom ϵ. It is seen that the sputtering yield per atom is roughly the same for all the three cases at $\epsilon < 1$ keV. The sputtering yield equal to one (runaway sputtering) is denoted by the dashed line. The dramatic increase of the sputtering yield at higher energies is illustrated in the inset.

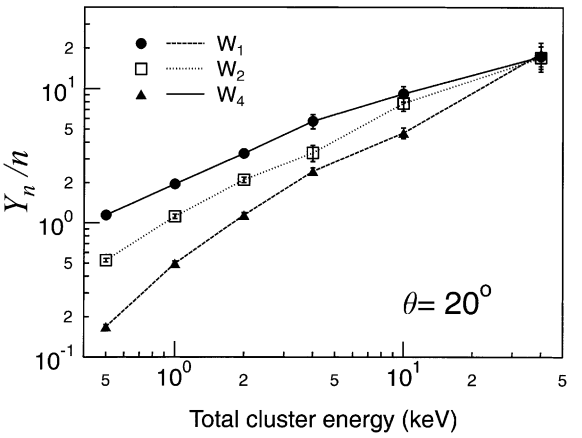

Fig. 3. W self-sputtering yields for the W_1, W_2 and W_4 bombardments ($\theta = 20°$), as a function of the total cluster energy E_{tot}. The twist angle was randomly selected for energies $\leqslant 2$ keV, whereas for cluster energies $\geqslant 4$ keV a fixed twist angle was used in order to avoid channeling.

$$Y_n(\epsilon) \sim nY_1(\epsilon), \tag{2}$$

to a good approximation (cf. Fig. 2). Upon impact the cluster fragmentates to n atoms with energies very close to ϵ each. The deposited energy density still remains too low for dense cascade formation and hence, enhancement of sputtering yields. This linearity, for $\theta = 20°$, breaks up at $\epsilon \sim 1$ keV.

As shown in the inset of Fig. 2, a dramatic enhancement of the sputtering yields by W_2 and W_4 bombardments is seen at $\epsilon > 2$ keV. The deposited nuclear energy is then large enough for the formation of a liquidlike region at the surface and ejection of agglomerates of atoms, consisting of up to tens of atoms. At $E_{tot} = 40$ keV the sputtering yields are roughly proportional to the number of atoms in the cluster

$$Y_n(E_{tot}) \sim nY_1(E_{tot}), \tag{3}$$

similarly to the studies by Colla et al. [19] of Au self-bombardment by small 16-keV clusters (see Fig. 3).

The fractions of sputtered species for 10 and 40 keV/cluster bombardment are given in Table 1. In all the cases single atoms are the predominant sputtered species. However, for increasing cluster sizes and energies the fraction of single atoms decreases and the fractions of larger sputtered clusters increase. It is relevant to ask whether impacts by clusters sputter away more clusters of the same type. If the cluster bombardment sputters on average more than one cluster of the same type, the redeposition of the atom cluster type can continue and even increase. However, if less than one cluster of the same type is sputtered, the distribution of redeposited species will move down to smaller cluster sizes.

Table 1
Fractions f_N of sputtered W_N species in simulations at total impinging cluster energies of 10 and 40 keV

Incident cluster	f_N					Largest (atoms)
	1	2	3	4	$\geqslant 5$	
W_1 (10 keV)	0.88	0.11	0.01	–	–	3
W_2 (10 keV)	0.76	0.22	0.02	–	–	3
W_4 (10 keV)	0.63	0.27	0.05	0.03	0.03	6
W_1 (40 keV)	0.84	0.14	0.01	–	0.01	5
W_2 (40 keV)	0.66	0.26	0.07	–	0.01	7
W_4 (40 keV)	0.55	0.26	0.06	0.04	0.09	32

N is the number of atoms in the sputtered clusters. The number of atoms in the largest cluster ejected from the surface at each case is also given in the table.

As the sputtered dimers were determined to be more stable in our test simulations than the tetramers, we concentrate here only on the ejection of W_2 species. At low redeposition energies the average number of dimers sputtered by an impinging dimer, Y^{W_2}, remains well below unity, ranging from 0.02 at 200 eV/cluster to 0.16 at 500 eV/cluster. The transition to self-sustaining dimer sputtering (i.e. when the number of ejected dimers on average is one) takes place between 2 and 4 keV/cluster ($Y^{W_2} = 0.56$ and 1.45, respectively). For the case of tetramer bombardment, we only note here that the average number of ejected W_4 by an impinging W_4 equal to one is reached only at 40 keV/cluster.

4. Discussion and conclusions

We have explored here a rather overlooked possibility of plasma-facing material erosion. While the clear advantage of W compared with low-Z materials, such as Be and C, is the low sputtering yield by hydrogen isotopes, self-sputtering yields for tungsten can pose a problem for continuous fusion device operation. On average the redeposition energies of W species will remain quite low. However, as the charge state distributions are quite broad [5,6], some redeposited species will have impact energies in the keV range.

Provided T_e is kept low enough to maintain redeposition energies $\leqslant 1$ keV, sputtering by clusters can be concluded to be less dangerous to the plasma-facing material lifetime and plasma contamination than by single atoms. As discussed above, the ability of cluster bombardment to self-sustain itself lies at rather high energies. If the impact energies remain at $\leqslant 2$ keV, bombardment by W_2 will eventually reduce to single-atom bombardment, whereas W_4 bombardment cannot sustain itself at all under conditions relevant for fusion devices.

The quadratic behaviour of the sputtering yield by clusters (Eq. (1)) as reported by Andersen et al. [18] for gold self-sputtering, was not observed for the tungsten clusters studied. One reason for this could be the lower cluster energies in our modeling than used in Ref. [18]. In the experiments, the lowest energy for which the quadratic behaviour was observed was roughly 60 keV/cluster. On the other hand, MD simulations by Colla et al. [19] did show the same linear dependence of the sputtering yield as obtained in our simulations. For gold this was observed already at 16 keV/cluster, while for tungsten this dependence is seen only at 40 keV/cluster. The reason for the difference in energy lies probably in the different physical characteristics of these metals. Not only is their lattice type different, but the melting temperature of tungsten is roughly three times higher than that of gold. We have recently shown that the melting temperature directly affects atom flow to surfaces in heat spikes [30], so a weaker effect in W is not surprising. The quadratic dependence of the sputtering yield is presumed to lie at higher energies, if present at all in tungsten.

In summary, we have studied the self-sputtering of W by small clusters ($n = 1, 2, 4$) in the energy range 0.2–40 keV/cluster. At energies relevant to fusion plasma-facing material redeposition ($E_{tot} < 1$ keV) the sputtering yields by single W atoms are higher than for dimers and tetramers. However, the sputtering yields by the W_2 and W_4 bombardments increase more strongly with increasing impact angle. At energies higher than 2 keV/atom, enhanced sputtering yields by the dimer and tetramer bombardments are observed. Similarly to MD studies of Au self-sputtering at 16 keV/cluster, sputtering yields proportional to the number of cluster atoms are observed at 40 keV/cluster.

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