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Section 2. Surface physics of materials exposed to plasmas

Molecular dynamics simulations of CH_3 sticking on carbon first wall structures

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Abstract

Tight-binding molecular dynamics simulations were used to obtain sticking cross-sections for CH_3 radical chemisorption on unsaturated carbon atom sites on carbon surfaces. Our results show that the chemisorption of a CH_3 radical is affected both by the angle of incidence of the radical and the local atomic neighborhood of the dangling bond. The sticking cross-sections are compared with experimental results and the implications of our modeling on C:T film growth in fusion devices are discussed.

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1. Introduction

A central problem in present-day fusion experiments is the selection of plasma-facing materials. Carbon is widely used as a material for fusion device walls in contemporary tokamaks and will be used in the high heat flux components of the divertor in ITER due to its outstanding thermal properties [1]. The main drawbacks with carbon are the high chemical erosion rate, even at low impact energies [2–6], and co-deposition with tritium.

It is known that the eroded species from carbon plasma-facing components form hydrocarbon films not only on the divertor plates, where prompt redeposition takes place, but also in other parts of the vacuum chamber [7,8]. Experiments carried out at the ASDEX Upgrade [8] resulted in the formation of both soft polymer-like C:H films (H/C ~ 1) and hard C:H films (H/C ~ 0.4). In order to successfully model and predict the performance of the next-step device, detailed knowledge about such film growth, especially the fundamental erosion and redeposition processes of hydrocarbon species, is of utmost importance.

The C:T film formation in fusion devices might be controlled by using a liner in the divertor pump duct [9] where neutral hydrocarbon radicals will be trapped or transformed before they can deposit in remote areas of the vacuum vessel. One of the most abundant sputtered radical species is the CH_3 radical [10,11], which is also known to be an important growth species in chemical vapour deposition growth of carbon films [12,13]. Recent experiments by von Keudell et al. [14,15] on surface processes between polymer-like C:H films and simultaneous methyl and atomic hydrogen beams have provided valuable information on the individual film growth mechanisms. Since the chemisorption of the impinging methyl radicals predominantly takes place on unsaturated carbon sites, the film growth can be characterized with a CH_3 sticking cross-section σ_s to these sites. The sticking cross-section can be thought as the effective area to which the CH_3 radical always chemisorbs upon impact.

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Using molecular dynamics (MD) simulations we study the chemisorption of thermal methyl radicals on unsaturated carbon sites on a hydrogen terminated diamond (1 1 1) surface. Several surfaces with different dangling bond configurations were examined in order to deduce what kind of dangling bond environment underlies the experimentally observed results. We also examine how the angle of incidence of the CH_3 radicals affects the sticking process. Our results are compared to experiments and the implications of our modeling on C:T film growth in fusion devices are discussed.

2. Simulation method

For the simulations of CH_3 radical chemisorptions on diamond (1 1 1) surfaces we employed the tight-binding (TB) method by Porezag et al. [16,17], which is known to describe well the chemistry in hydrocarbon systems. The model was tested in both the self-charge-consistent (SCC) and non-SCC modes. Since the results were roughly the same for both cases, the non-SCC modification was used in most sticking simulations. This reduced the calculation time significantly.

A diamond lattice consisting of two layers of carbon with a total of 120 atoms, was used as the chemisorption substrate. Both (1 1 1) surfaces were hydrogen terminated and an unsaturated carbon atom site was created by removing one hydrogen atom from the surface (see Fig. 1(a)). The surface temperature was 0 K in all of the simulations.

The effects of atoms neighboring an unsaturated carbon atom site were studied in four cases. From the first lattice with one dangling bond (cf. Fig. 1(a)), a second lattice with seven dangling bonds at the surface was created by removing the hydrogen atoms neighboring the original dangling bond (Fig. 1(b)). In order to study a completely bare dangling bond, a third lattice with an unsaturated carbon atom site on top of a four carbon atom cluster was created (Fig. 1(c)). On the fourth surface, hydrogens surrounding the dangling bond were replaced by three methyl groups (see Fig. 1(d)). This surface allowed us to study a partly shielded dangling bond.

A CH_3 radical was created above the surface and the distance between the surface and the radical was set to be larger than the effective interaction range of the model. The radical was directed toward the surface in a selected off-normal angle of incidence, with the translational

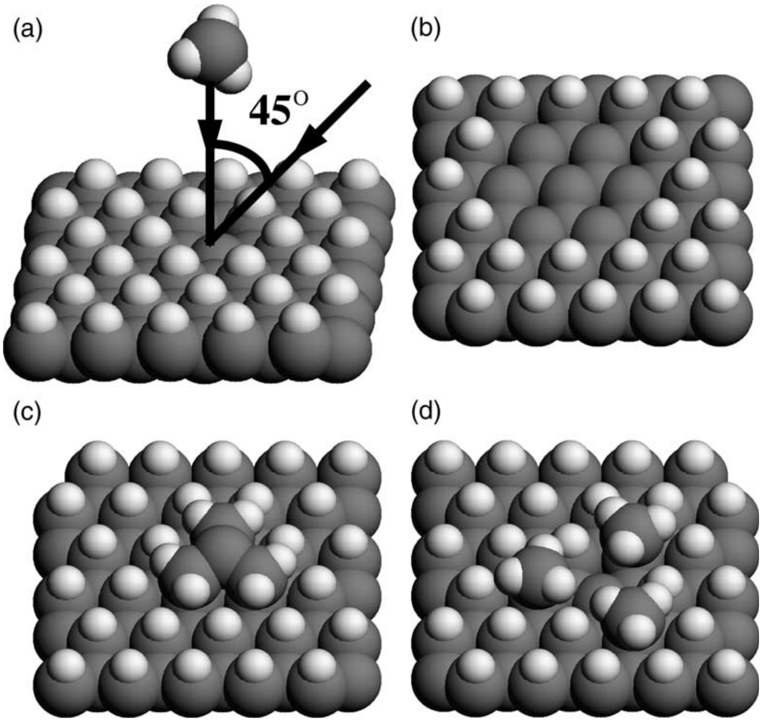

Fig. 1. Illustrations of four diamond (1 1 1) surfaces used in our modeling, with one (a) and seven (b) unsaturated carbon atoms, a four carbon atom cluster (c) on top of the surface (three of these carbon atoms being terminated by hydrogen) and with three methyl groups (d) neighboring the dangling bond seen at the middle of the surface. The dark spheres represent carbon atoms and the light ones hydrogen atoms. The incoming methyl radical is directed toward the surface in a normal and 45° angle of incidence in the case (a).

velocity, and rotation and vibrational motion corresponding to a temperature of 2100 K. Radicals in normal angle of incidence were simulated for all surfaces, but in order to study the angular dependence on the sticking cross-section we used the surface with one dangling bond also for simulations of radicals arriving with a 45° angle of incidence. The impact simulations were followed for 500 fs, after which the final bonding configuration was examined.

The impact points were chosen randomly inside circular segments, centered on the dangling bond site, with a radial width $\Delta r = 0.1$ Å each. This is a stratified Monte Carlo (MC) strategy, which has in similar context been shown to give accurate results more efficiently than the conventional MC [18,19]. The maximum distance of an impact point from the dangling bond site was 3.0 Å. The sticking cross-sections were obtained by running series of impact simulations for the segments and integrating over the corresponding sticking probabilities. In the case of seven dangling bonds only chemisorptions to the central unsaturated carbon site were taken into account.

3. Results

The most common reaction process for the incoming methyl radical was to chemisorb onto a dangling bond or to react with the surface hydrogen to form a volatile CH_4 molecule. Besides these two cases, we also observed some unusual bonding configurations in which the CH_3 group decomposed, as one or two of its hydrogen atoms chemisorbed onto dangling bond sites at the surface and the remaining CH_x group chemisorbed onto some other dangling bond sites. In some cases one of the hydrogen atoms in CH_3 chemisorbed onto a dangling bond site and the remaining part, a methylene (CH_2) radical, drifted away from the surface. These were observed with the surface with seven dangling bonds, but also in the case of 45° angle of incidence at the one dangling bond surface.

The sticking cross-section obtained for the surface with one dangling bond, at normal incidence, was $\sigma_s = (10.4 \pm 1.2)$ Å^2. Compared with the area per surface site ($\sim$5.7 Å^2), this is a quite large value (cf. Fig. 2). The large cross-section is explained by the observation that CH_3 radicals impinging even at a rather large distance from the unsaturated carbon atom were deflected from the surface hydrogen and in some cases directed towards the dangling bond. When the angle of incidence was changed to 45°, a sticking cross-section of $\sigma_s = (7.5 \pm 1.6)$ Å^2 was obtained.

The sticking cross-section obtained for the surface with seven dangling bonds was about half of the value obtained for the single dangling bond configuration, $\sigma_s = (6 \pm 2)$ Å^2. Since methyl radical chemisorptions occurred in all of the simulations, and only chemisorptions onto the central dangling bond were taken into account, the obtained σ_s corresponds to the area per one dangling bond site at the surface, 5.7 Å^2.

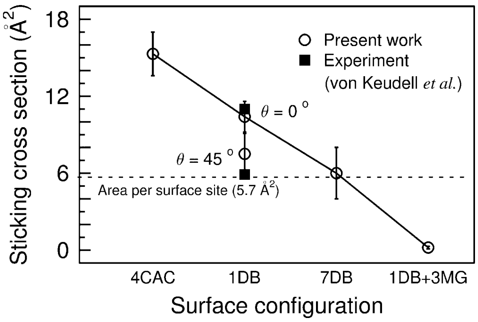

Fig. 2. Sticking cross-sections obtained using the TB model for different surface configurations, a four carbon atom cluster (4CAC), one dangling bond (1DB), seven dangling bonds (7DB), and one dangling bond surrounded by three methyl groups (1DB + 3MG) at the surface, and for different angle of incidence for the CH_3 radicals, are compared with the experimentally obtained values as well as the area per surface site (5.7 Å^2).

On the third surface (cf. Fig. 1(c)) there were no steric hindrances for the chemisorption of a CH_3 radical. As expected, the sticking cross-section obtained with this configuration was even higher than for the case of one dangling bond, $\sigma_s = (15.3 \pm 1.7)$ Å^2.

The sticking cross-section obtained for the fourth surface (Fig. 1(d)) was $\sigma_s = (0.2 \pm 0.1)$ Å^2. In this case the neighboring methyl groups shield the dangling bond from the incoming radical, resulting in very few chemisorptions.

4. Discussion

The values of sticking cross-sections obtained in our simulations compare well with experimentally determined values. In the experiments by von Keudell et al. [14,15,20], sticking cross-sections of $\sigma_s = 11$ Å^2 for normal angle of incidence, and 5.9 Å^2 for 45° angle of incidence were obtained from complex rate equations, employing various experimentally determined parameters. The experimental values are averages over all the cross-sections, since there are many types of surface sites. In these experiments the sample was not diamond-like carbon but polymer-like hydrogenated carbon, where the average number of neighboring carbon atoms is smaller and the shielding of the unsaturated carbon atom site can therefore be assumed as quite low. Of all the cases studied, the surface with one dangling bond corresponds best to the case of polymer-like C:H. Both of the experimental values agree well with our results for the surface with one dangling bond, (10.4 ± 1.2) Å^2 and (7.5 ± 1.6) Å^2 for normal and 45° angle of incidence, respectively (see Fig. 2). This strongly supports the experimental evidence that the sticking process is angle dependent. However, if the dangling bond coverage is large, the sticking cross-section will be affected by neighboring unsaturated carbon atom sites and the chemisorption events can no longer be described as independent of each other. This is seen in the case of seven dangling bonds, for which the sticking cross-section is a factor of ~1.7 lower than for the case of one dangling bond.

It is known that deposited hydrocarbons can be both neutrals and ions and that most of these will have energies between 1 and 10 eV. It has also been observed that the H/C ratio in hydrocarbon films can vary from ~0.4 for hard films to ~1 for polymer-like films. All these aspects have to be taken into account in studies of hydrocarbon sticking processes. The results presented in this paper show that the sticking cross-section is strongly affected both by the neighborhood of an unsaturated carbon atom site and the angle of incidence for the incoming radicals. Hence it is questionable whether using a single value of the CH_3 sticking coefficient (as frequently done, see [21–23]), is sufficient to describe methyl radical chemisorption in the different cases.

5. Conclusions and outlook

Methyl radical chemisorptions on unsaturated carbon atom sites on diamond (1 1 1) surfaces with different surface configurations were calculated using TB MD simulations. Our results show that the CH_3 radical chemisorption is affected both by the local atomic neighborhood of the dangling bond and the angle of incidence of the radical.

Simulations of the sticking of other C_xH_y species and at higher impact energies are under preparation. Also, the observation that radical fragmentation and unusual adsorption configurations appear to be more pronounced at larger angle of incidence requires further study.

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