

Molecular dynamics simulations of C_2 , C_2H , C_2H_2 , C_2H_3 , C_2H_4 , C_2H_5 , and C_2H_6 bombardment of diamond (111) surfaces

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Abstract

The sticking and erosion of C_2H_x molecules (where $x = 0-6$), at 300 and 2100 K onto hydrogenated diamond (111) surfaces was investigated by means of molecular dynamics simulations. We employed both quantum-mechanical and empirical force models. Generally, the sticking probability is observed to somewhat increase when the radical temperature increases and strongly decrease with increasing number of H atoms in the molecule.

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1. Introduction

Understanding the erosion of hydrogenated carbon-based films are of fundamental importance for fusion applications like ITER. Diamond and materials with diamond-like structures are important in many technological applications because of their unique mechanical, chemical and optical properties [1,2]. They are especially important for future fusion devices [3–5] since carbon is a major candidate as a plasma-facing material. The plasma-facing component lifetime and the contamination of the plasma will be determined by the erosion mechanisms and their rates, but also by the transport and the re-deposition of eroded material. Hydrocarbon species are released via physical and chemical sputtering when deuterium- and tritium ions and neutrals, which have escaped from the fusion core plasma, interact with carbon-based first walls. These radicals may later redeposit onto the divertor tiles but also in other regions of the vacuum chamber which are not in direct contact with the fusion plasma [6,7]. Due to the fact that tritium is bound in these hydrocarbon films, is highly

radioactive and cannot easily be recycled, the achievement of a good control over these deposited hydrocarbon films is of great importance. Detailed knowledge about hydrocarbon film growth, especially about the fundamental erosion and redeposition processes of hydrocarbon species, is needed in order to successfully model and predict the performance of the next-step device.

By the means of molecular dynamics (MD) simulations we have examined the sticking process of a number of hydrocarbon molecules impinging onto a hydrogenated diamond (111) surface with one and seven dangling bonds, impinging at normal angle of incidence at different energies. Sticking probabilities and cross sections have been calculated for all cases, and the nature of the sputtered species have been examined.

2. Simulation method

In this section we describe the methodology used to study sticking and erosion of small hydrocarbon molecules at hydrogenated diamond (111) surfaces.

The diamond lattice used in our simulations as a chemisorption substrate consisted of two layers of carbon atoms (in total 120 atoms). Both (111) surfaces were hydrogen

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terminated and a carbon atom site was created by removing one hydrogen atom from the surface. The surface temperature prior to the hydrocarbon molecule bombardment was 0 K in all our simulations. For a more detailed description of the creation of the substrate, see Ref. [8].

A C_2 , C_2H , C_2H_2 , C_2H_3 , C_2H_4 , C_2H_5 , or C_2H_6 molecule was created and placed above the diamond surface with a distance between the radical and surface larger than the effective interaction range in the model. The radical, having translational velocity, rotational and vibrational motion corresponding to a selected temperature, was directed in normal angle of incidence to a randomly chosen point on the surface. According to a stratified Monte Carlo (MC) strategy, the impact points on the surface were chosen randomly inside circular segments with a radial width of $\Delta r = 0.1 \text{ \AA}$ each and centered on the dangling bond site. This has been shown to give accurate results more efficiently than conventional MC (i.e., completely arbitrary impact points on the whole surface) [9,10]. The fraction of cases in which sticking occurred in each segment provides the sticking probabilities for different distances in Figs. 3 and 6.

The maximum distance of an impact point from the dangling bond site was 3.0 \AA . The sticking cross section is obtained by MC integrating [9] the sticking probability over the surface. After running a series of impact simulations for each segment one can, with the knowledge of sticking probabilities and surface areas of the segments, carry out the integration.

Molecules which were bound to an unsaturated carbon atom by covalent bonds at the end of the simulation were considered chemisorbed. The simulations were followed for 1 ps (since tests with longer simulation times verified that 1 ps simulations were adequate to determine the chemisorption of an incoming radical). However, for C_2H_4 a longer time of 2 ps was used since in a small portion of the simulations the molecule entered into a short lived metastable state where one of the carbon atoms was close to the unsaturated site but not bonded to it. For other molecules no such behaviour was observed. After this the final bonding configuration, and the sputtered species were examined.

2.1. Inter-atomic potentials

Both tight-binding (TB) [11,12] and empirical [13] hydrocarbon force models have been employed in our simulations, when C_2H_x (where $x = 0-6$) molecules impinged onto hydrogenated diamond (111) surfaces. The chemistry in C–H systems is well described in both of these models. The empirical Brenner potential [13], is computationally less intensive which allows one to achieve more comprehensive statistics in MD simulations, while still describing bond formation and breaking correctly. The potential cut-off was 2.46 \AA , as results obtained using this value has been shown to be more reliable than with the original cutoff [8]. TB is based on a second order expansion of the Kohn–

Sham total energy in density functional theory with respect to charge density fluctuations. This method gives a quantum-mechanical representation.

3. Results

3.1. Classical simulations

The most common reaction mechanism for the incoming molecule was either to stick to the surface or to be repelled. In Fig. 1 the most typical final sticking configurations for the different molecules investigated have been visualized. The C_2H_6 case is not shown because no sticking was observed for this molecule.

In Fig. 2 the sticking cross sections calculated for all different molecules impinging onto a diamond (111) surface with one unsaturated carbon atom site is depicted. The general view is that the sticking cross section decreases when the hydrogen content of the C_2H_x ($x = 0-6$) molecule is increasing.

With the classical model we were able to analyze sticking profiles for all the species with good statistics. These profiles are depicted in Fig. 3(a) (300 K) and (b) (2100 K). In

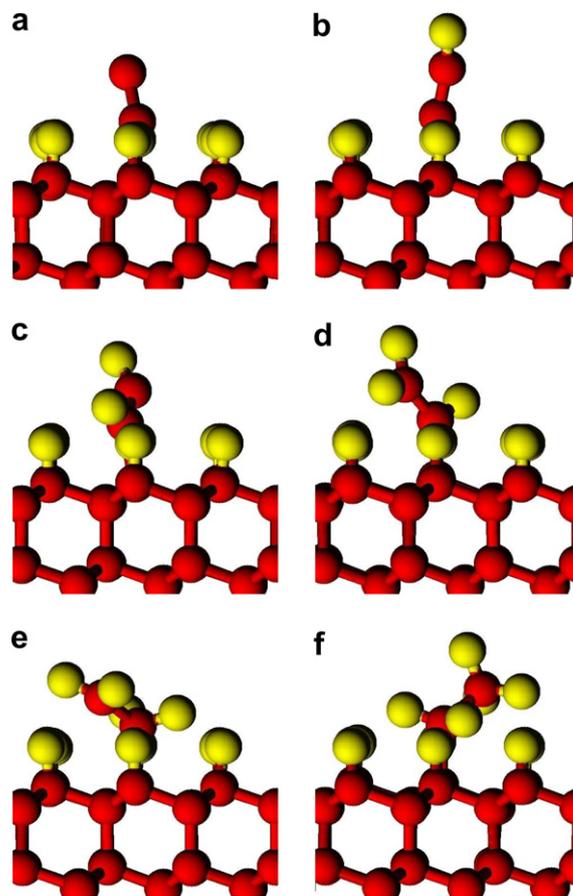


Fig. 1. Snapshots of final sticking configurations for a (a) C_2 , (b) C_2H , (c) C_2H_2 , (d) C_2H_3 , (e) C_2H_4 , (f) C_2H_5 molecule on a hydrogenated diamond (111) surface with one unsaturated carbon atom site. The light spheres are hydrogen and the dark spheres are carbon.

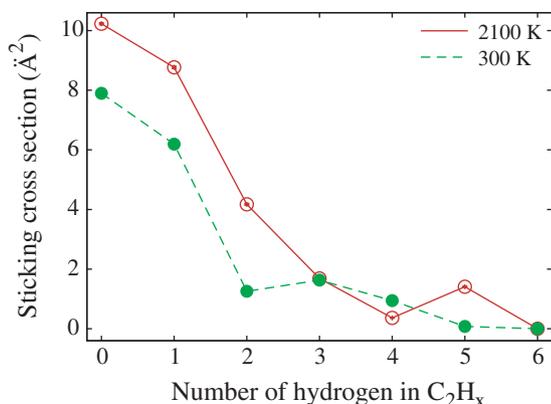


Fig. 2. Sticking cross sections obtained from simulations with one unsaturated carbon site at the surface, and different molecules C_2H_x , where $x = 0-6$, impinging at 300 and 2100 K.

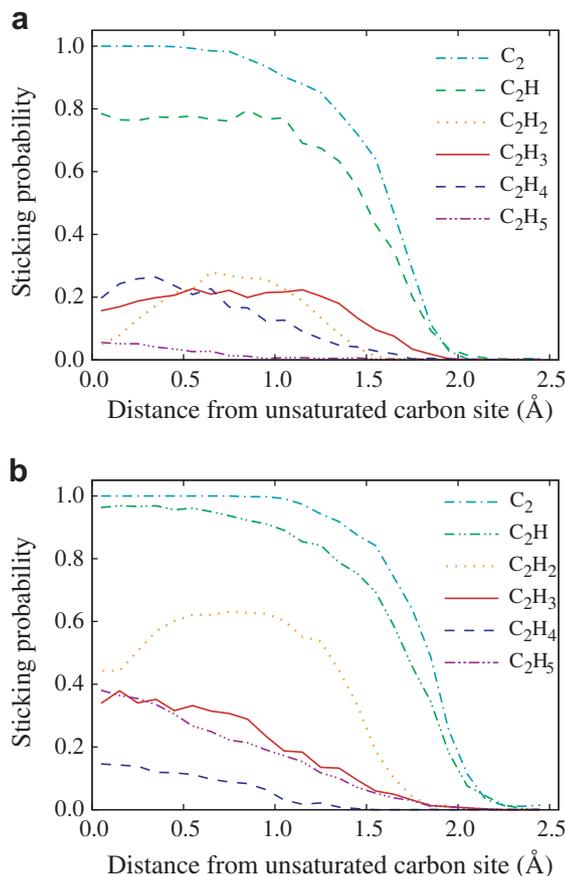


Fig. 3. Sticking probability vs. distance from the unsaturated carbon site on the hydrogenated diamond (111) surface, as obtained with the classical model, for (a) 300 K and (b) 2100 K. The sticking probability was zero for the C_2H_6 case.

the simulations with C_2H_6 , we observed no sticking cases, which is why there is no profile for this molecule in Fig. 3. In all cases, except for in the C_2H_2 case, the sticking probability approaches zero when the impact point of the molecule is moved further away from the unsaturated carbon atom site. In the C_2H_2 case, the maximum in the

sticking probability is reached when the molecule is impinging onto the surface at a distance of ~ 0.7 Å from the unsaturated carbon site.

We also did a minor investigation of how the sticking probability is affected when a surface with 7 unsaturated carbon sites (one unsaturated site surrounded by 6 others) is used. This was done for the cases of C_2H_2 , and C_2H_5 molecules impinging on to the surface. The variation of different resulting surface configuration was huge. First of all, the sticking probability is highly affected by the rotation of the molecule. In several cases when the molecule approached the surface as a plane horizontal to the surface, the outcome of the simulation was reflection. Secondly, the molecule can either stick to one or two of the unsaturated carbon atom sites, or first stick to one unsaturated site, then move on the surface and stick to another unsaturated carbon atom site. The analysis of these complex bonding configurations was therefore difficult. In Fig. 4 we have depicted the potential and kinetic energy as a function of simulation time for one case, where a C_2H_2 is chemisorbed onto two unsaturated carbon atom sites on the surface.

3.2. Tight-binding simulations

Using the TB approach, we were able to investigate the detailed behavior of a C_2H_2 molecule reacting with the surface with one unsaturated carbon atom site. The distance dependence of the sticking cross section differs somewhat from those obtained with the classical model. The sticking probabilities as a function of distance from the unsaturated carbon atom site are depicted in Fig. 5. The sticking cross sections for C_2H_2 molecules at 300 and 2100 K obtained using the TB and the classical approach are visualized in Fig. 6. When the temperature is lower (300 K), we get a larger sticking cross section from the TB simulations than from the classical. At higher (2100 K) temperature, the relation is the opposite (see Fig. 6). However, the overall difference between the TB and classical values is still clearly smaller than the order-of-magnitude differences between different hydrocarbons (cf. Fig. 2).

4. Discussion

In our simulations we saw a general trend of decreasing sticking cross sections for increasing number of hydrogen in the C_2H_x ($x = 0-6$) molecule. This is of no surprise, since the more hydrogen the molecule has, the more easily the molecule will be reflected due to the shielding of both the hydrogen parts of the molecule and the hydrogen atoms surrounding the unsaturated carbon atom site at the surface. The decrease is, however, not monotonous. This is because molecules with an odd number of H have an unpaired electron, which makes them more reactive.

This finding is similar to the results of Ref. [14]. The reflection coefficients of these hydrocarbon species showed a decreasing trend with increasing energy. Since Ref. [14] used amorphous sample surfaces and calculated reflection

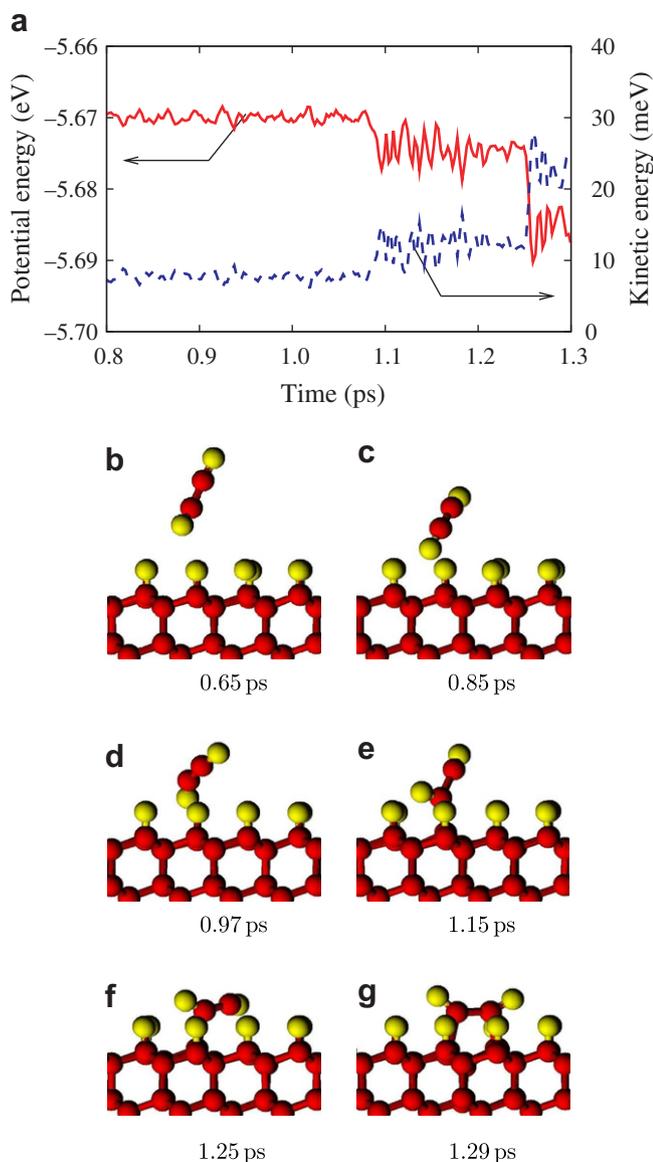


Fig. 4. (a) Evolution of potential and kinetic energies of the system (molecule and substrate) for a typical C_2H_2 sticking case. As a bond is formed, some of the potential energy is converted to kinetic energy. Snapshots of the molecule under the same period of time are depicted in (b–g). The light spheres are hydrogen and the dark spheres are carbon.

coefficients, a direct comparison of the quantitative results cannot be done.

In all our simulation cases, except for in the classical C_2H_2 case, the sticking probability was observed to monotonously approach zero when the impact point of the molecule moved further away from the unsaturated carbon atom site. This is natural, since hydrogen atoms surrounding the unsaturated carbon site at the surface are preventing the incoming molecule from sticking when the impact point for the molecule moves further away from the unsaturated carbon site. In the C_2H_2 case, however, the symmetry of the molecule will cause an enhanced sticking probability after a certain distance (if it hits at the midpoint of the dangling bond, a stable bond to only one of the C atoms is not likely to form), and the maximum in the stick-

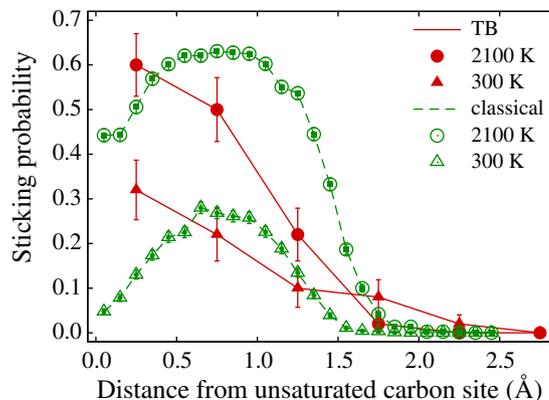


Fig. 5. Sticking probability vs. distance from the unsaturated carbon site on the hydrogenated diamond (111) surface, as obtained with the tight-binding model for C_2H_2 molecules impinging at 2100 K and 300 K.

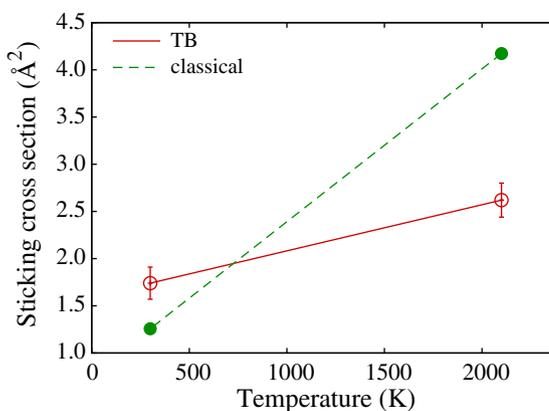


Fig. 6. Temperature (K) sticking cross sections for C_2H_2 as obtained from the TB and classical simulations.

ing probability in the classical simulations was seen to be reached when the molecule was impinging onto the surface at a distance of ~ 0.7 Å from the unsaturated carbon site. The fact that this effect was not observed in the TB simulations indicates that the additional flexibility provided by the quantum-mechanical model may remove this geometrical effect.

One explanation for the increased sticking probability for radicals with higher energies (2100 K vs. 300 K) is that the original molecule can break up, allowing the fragments to stick to the surface more readily. Hydrogens at the surface are more likely to be sputtered away when the radicals are impinging onto these with higher energies than with lower energies, which also makes it easier for the radicals to chemisorb to the surface.

5. Conclusions

We have investigated sticking and erosion of hydrocarbon species onto hydrogenated diamond (111) surfaces. Generally, the sticking probability is observed to increase when the radical temperature increases and strongly decrease when the numbers of hydrogen atoms in the molecule increase.

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