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Molecular dynamics simulation of the impact behaviour of various hydrocarbon species on DLC

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Abstract

We have investigated the sticking and H-abstraction behaviour of various hydrocarbon species relevant for the growth of thin diamond-like carbon films (DLC) by means of molecular dynamics (MD) simulations, using the updated Brenner potential. These species include C_2, C_2H, C_3, propynylidene (i.e. linear C_3H), cyclopropynyl (i.e. cyclic C_3H) and cyclopropenylidene (i.e. cyclic C_3H_2), with low kinetic energies typical for remote type plasma sources.

We demonstrate and explain the different reactivities of these species at the surface (i.e. sticking efficiencies), as well as their ability to remove hydrogen from the surface (i.e. abstractions efficiencies).

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1. Introduction

Diamond-like carbon (DLC) films have become technologically important materials, used in electronic applications, e.g. as antifuses, and in mechanical applications, e.g. as protective coatings or biocompatible coatings [1]. Depending on the desired properties, different types of DLC can be produced. A continuous effort is being made to prepare DLC films having an sp^3 fraction as high as possible. It is generally accepted that the mechanism for the formation of an sp^3-rich DLC layer is through subplantation [1]. This mechanism, however, requires the sub-surface implantation of C-containing species, and thus a flux of high-energy particles, leading to physical growth of the layer. It would be desirable to develop a source to produce DLC layers having a high sp^3/sp^2 ratio with high growth rates from low energy particles. Remote plasma sources, as for example the expanding thermal plasma (ETP), show promising results [2]. Computational modeling of the processes occurring at the substrate in these types of deposition systems can elucidate the mechanisms leading to the formation of these rapid-growing, sp^3-rich DLC layers. Besides, no experimental method exists for the determination of the

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microscopic structure of the deposited layer in three dimensions. Hence, simulation methods are an invaluable tool to investigate the deposition process and the resulting film characteristics.

In Section 2, a brief description of the model will be presented. Next, the results will be shown, focussing on the specific role and effect of the different possible growth species. Finally, a summary and a conclusion will be given.

2. Description of the model

The model used in this work was initially developed by Abrams and coworkers [3], and subsequently modified, mainly regarding the interatomic potential. The model now makes use of the updated Brenner potential [4].

In an MD model, the atoms in the system are traced by Newtonian mechanics. The force acting on each atom in this system is calculated from the analytical derivative of the interatomic potential. Then, the atom's trajectory is calculated using the velocity Verlet scheme [5], at a constant temperature, using the Berendsen heat bath [6].

Periodic boundary conditions were enforced in the $\pm x$- and $\pm y$-directions. An invariable timestep of 0.5 fs was used throughout the simulations. For each condition (i.e. different species with different energies), 500 impacts were performed. Each impact was normal to the substrate, at a random $\{x, y\}$ position. Also the orientation of the impinging molecule relative to the surface was chosen randomly.

Instead of using a 'perfect' surface, such as a clean diamond surface, we chose to perform the simulations on a previously simulated DLC layer, to investigate the role of the different species during the growth of the layer. This DLC layer contained 830 atoms, of which the lower 126 atoms were kept static to anchor the simulation cell and to simulate a thick substrate. After deposition, this layer was relaxed at a temperature of 300 K.

To investigate the influence of the species energy on their deposition behaviour, the species were given a kinetic energy of 1 eV and 0.1 eV. Every particle impact was followed during 2500 time steps (1.25 ps) for the 1 eV kinetic energy impacts, and during 5000 time steps (2.5 ps) for the 0.1 eV kinetic energy impacts.

The species were selected on the basis of threshold ionisation mass spectrometry (TIMS) [7] and cavity ring-down spectroscopy (CRDS) measurements [2]. These measurements indicate that a whole range of species is present in the discharge. However, the specific behaviour of these different species when hitting the surface is still unclear. Information regarding the ETP source and CRDS measurements can be found in [2] and references therein.

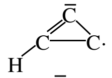
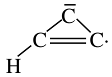
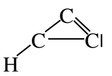
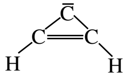
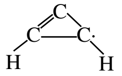
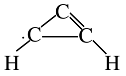
In the present simulations, we have focussed on the sticking and H-abstraction characteristics. The species included here are C_2, C_2H, linear C_3, linear C_3H (i.e. propynylidyne), cyclic C_3H (i.e. cyclopropynyl) and cyclic C_3H_2 (i.e. cyclopropenylidene).

3. Results and discussion

In view of explaining how and why the different species show a different reactivity on the DLC substrate, it is important to first consider their structure. In Table 1, the species are presented, together with their structure. All major resonance contributors are shown. It should be noted, that in a classical MD model, resonance contributors and electrons are not taken into account directly. However, the Brenner potential models the species and the chemical reactions realistically, in such a way that they correspond to the physical reality of resonance contributors and electrons. Therefore, the results in the following discussion are explained in physical terms, following directly from the model results.

The processes observed in these simulations are sticking, H-abstraction and reflection. Note that etching of C-containing species did not occur. In Fig. 1, the sticking efficiency of the different species is plotted for two different values of their initial kinetic energy. Note that at both 0.1 eV and 1 eV, all species stick to the surface with only one atom, in more than 90% of the sticking events. However, sticking with two carbon atoms also occurred, especially for C_3H_2. All investigated species show a sticking efficiency value between 0.1 and 0.4.

Table 1
Overview of the selected species investigated in the present work, as well as their major resonance contributors

Species	Resonance contributors		
C_2	|C=C|	·C≡C·	
C_2H	|C=Ċ–H	·C≡C–H	
C_3	|C=C=C|	·C≡C–Ċ|	|Ċ–C≡C·
C_3H	|C=C=Ċ–H|	|C=Ċ–C̄–H	·C≡C–C̄–H
Cyclic C_3H			
C_3H_2			

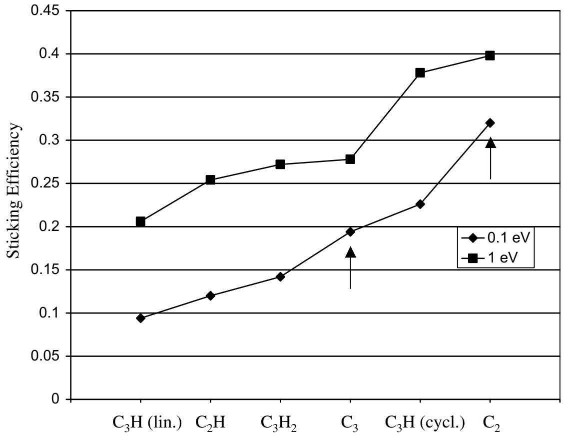


Fig. 1. Calculated sticking efficiency of the different species plotted for two different initial kinetic energies.

It can be seen in the figure that the sticking efficiency of the species that do not contain hydrogen decreases less with decreasing energy than the species which contain hydrogen (marked with an arrow). The reactivity of the species is determined by their unpaired electrons, since their kinetic energies are too low to break double or triple bonds at the surface, in order to create unpaired electrons at the surface. This is also obvious from the figure, e.g. by comparing the reactivity of C_2 to C_2H. The C_2 radical, which has two unpaired electrons in one of its resonance contributors, is the most efficient sticking species. The reactivity of C_2H is about half compared to C_2. Indeed, due to the H-atom on one of the C-atoms, only the other C-atom remains reactive. Also, the H-atom leads to steric hindrance: in order to stick to the surface, the unpaired electron of the C_2H radical must be pointing towards the surface. The C_2 radical, on the other hand, does not require a certain orientation relative to the surface, since one of the two unpaired electrons will be available at all times.

The same effect can been seen in C_3: it has three major resonance contributors, as shown in Table 1. In none of the C_3 sticking events, the middle carbon atom is involved, indicative for the reactivity of the two other atoms (cf. [8]).

On the other hand, in the C_3H_2 molecule, only the H-free C-atom shows high reactivity. Nevertheless, at 1 eV it has almost the same reactivity as C_3. With decreasing kinetic energy, its reactivity decreases steeply. This is a result of the structural instability of this molecule: when it hits the surface, it easily breaks up creating unpaired electrons, hence boosting its reactivity. Decreasing its kinetic energy sharply lowers the probability of breaking up, thereby decreasing its reactivity.

In Fig. 2, the H-abstraction efficiency is illustrated. In this figure, C_3 and C_3H are not shown as they do not cause any desorption of hydrogen from the surface during their impacts. It can also be seen that while C_2 is an effective sticking species, it has a low H-abstraction efficiency, making this species a good 'growth species'. None of the species etches carbon atoms from the surface. As a general trend, the desorbing species mostly consists of the impinging molecule to which a surface H-atom is bound.

Finally, another important factor is the number of H-atoms brought to the surface and the number of H-atoms removed from the surface. It is found

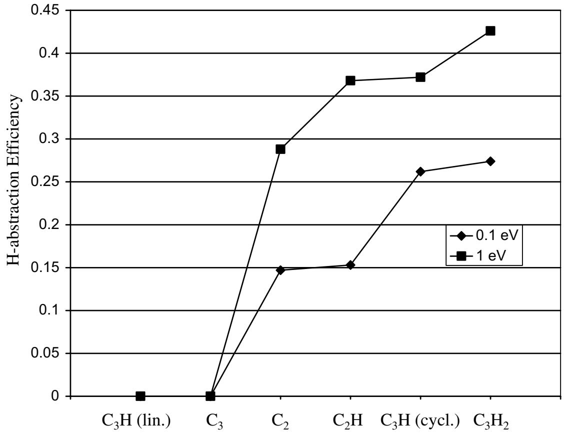


Fig. 2. Calculated H-abstraction efficiency of the different species plotted for two different initial kinetic energies.

that C_2 only removes H, C_3 does not bring H to the film, nor does it remove H from the film, and the linear C_3H molecule only adds hydrogen to the surface. For the other species, the H_{out}/H_{in} ratio is found to be 0.75 for C_2H, 0.87 for cyclic C_3H and 0.62 for C_3H_2 (at 1 eV kinetic energy), thus effectively bringing more H into the film than removing H from the film. Therefore, it can be concluded that films deposited mainly by C_2, C_3 and cyclic C_3H will contain less hydrogen than films deposited by C_2H, linear C_3H and C_3H_2.

4. Summary and conclusion

In view of the current interest in the impact behaviour of small radical species in the remote thermal expanding plasma source, we have simulated their impact using classical MD simulations.

It has been shown that the reactivity of these species is directly linked to their structure in three ways, i.e. their unpaired electrons (e.g. C_2), steric hinderance (C_2 versus C_2H and C_3 versus C_3H) and stability on impact (C_3H_2).

We also considered their ability to etch H from the surface. While C_3 and C_3H do not remove H-atoms from the surface, the other species investigated can easily abstract H from the surface, leading to H-abstraction efficiency values up to 0.43. Since only C_2 does not bring H to the surface, and only removes H from the surface, it is the only species that effectively decreases the H-content in the film. The present study is of interest mainly for remote type plasmas containing these kind of radicals.

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