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What makes a dangling bond a binding site for thermal CH_3 radicals? — A combined molecular dynamics and potential energy analysis study on amorphous hydrocarbon films

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ABSTRACT

Identification of dangling bonds on amorphous films is not as straight forward as in the case of crystalline materials. The task is further complicated in the case of amorphous hydrocarbon (a-C:H) films by the existence of a wide variety of atomic arrangements. We present a technique based on potential energy analysis of a-C:H films to identify dangling bonds and physisorption sites. However, molecular dynamics simulations of the sticking of thermal CH_3 on a-C:H surfaces show that not all dangling bonds are binding sites for a CH_3 radical. Furthermore, the total sticking coefficient of the surface is not solely linked to the number of dangling bonds and can even decrease for the same number of dangling bonds because the carbon atoms that possess a binding site, *active carbon atoms*, show drastically different reactivity towards CH_3. The reactivity of active carbon atoms is decided by (a) their type, which is decided by the bonding partners, (b) their distance from the local surface and (c) the local environment. The reactivity of the active carbon atoms can be largely increased by energetic ion bombardment due to hydrogen depletion and local rearrangement.

1. Introduction

Amorphous hydrogenated carbon (a-C:H) films – often also termed diamond-like carbon films – are a fascinating class of amorphous materials with an amazing variety of forms and physical properties [1,2]. The great interest in these types of films was and is triggered by their extraordinary material properties which are of great interest for a wide range of technological applications such as protective coatings in magnetic storage technology [3–5], tribological coatings in the automotive industry [5], optical coatings [6], and quite importantly as bio-compatible coatings for various medical applications [5,7]. These films are routinely manufactured using plasma-enhanced chemical vapor deposition from hydrocarbon precursor gases [2,8,9]. Similar conditions prevail in the cold edge of magnetically confined nuclear fusion plasmas where also the growth of hydrocarbon films was observed due to the erosion of carbon first-wall materials [10,11].

In such low-temperature plasmas the precursor gas is ionized and dissociated, and carbon-carrying radicals and ions as well as hydrogen atoms and ions impinge on the surface [8,12]. The observed film growth is the net result of various deposition and erosion processes triggered by the different particle species. These processes are not entirely independent and clear evidence for the existence of synergisms has been found [13]. For example, in particle-beam experiments using independently controllable radical sources for atomic hydrogen atoms and CH_3 radicals it was shown that the simultaneous interaction of both species leads to a much higher sticking probability for the methyl radical than irradiation with CH_3 alone [12,14,15]. Similarly, ion bombardment was also found to increase the sticking probability of CH_3. These results were explained by the abstraction or displacement, respectively, of surface atoms, thereby creating an active surface site, often termed a *dangling bond*. The CH_3 radicals are assumed to directly stick on these dangling bonds. In this picture the steady-state dangling bond coverage of the surface determines the sticking probability of CH_3 and thus the growth rate. Rate equation models that account for the dangling bond creating and consuming processes could very well reproduce the growth rates in the parameter range investigated in these experiments [13,16–18].

Modeling the evolution of the structure during the a-C:H film growth is inherently a multi-scale problem. Monte Carlo (MC) methods with parametrized sets of reaction probabilities for various processes involving both CH_3 radicals and ions have been used in the past to model the film structure [19–22]. The reaction probabilities are derived based on the input from both experiments and lower scale models such as molecular dynamics and ab initio calculations. Ab initio calculations are able to model the formation and the electronic structure and properties of dangling bonds on well-defined surfaces of a few atoms [23,24]. For amorphous film growth this will not be representative due to the large number of atomic arrangements. Molecular dynamics (MD) simulations can bridge this gap by still resolving dynamic details of the atomistic processes while being able to treat considerably larger systems and hence provide the required input for the structural MC growth models.

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MD simulations have been used extensively in the past for studying the sticking of hydrocarbon radicals on a-C:H surfaces [25–35]. The influence of the orientation of the radical was studied by Sharma et al. [36]. The effect of hydrogen flux on the sticking probabilities of hydrocarbon radicals on a-C:H surface was investigated by deRooij et al., using the Brenner potential at 700 K and 1000 K sample temperatures [29]. The sputtering and deposition of hydrocarbon films by C_2H_2 radicals were studied by Jäger et al. at high impinging energies of the radical [35]. The intrinsic stress generated due to ion bombardment was also investigated in such films [33,34]. The growth of diamond-like carbon films from different low energy (<2 eV) radical species, mainly C_2H_2, was investigated by Neyts et al. using the Brenner potential [30].

The sticking cross-section for the chemisorption of methyl radicals on specific dangling bond locations on the diamond surface were studied by Träskelin et al., using both classical MD and a tight binding approach [37–39]. In these simulations a dangling bond was created by removing a hydrogen atom from a fully hydrogen-terminated surface.

It was shown that the cross-section depends on the local environment of the dangling bonds. The simulations also showed that for low energy radicals (corresponding to a thermal distribution of 2100 K distribution) no sticking was observed on the fully hydrogen terminated surface.

MD simulations of the sticking probability of CH_3 radicals on reconstructed diamond surfaces were performed by Alfonso et al. [40,41] for energies above 1 eV at different incident angles. It was observed that the sticking probability increases with the incident energy and reduces with both the angle of incidence with respect to the surface normal and the surface hydrogen content. The decrease of sticking probability with surface hydrogen content was explained by the reduction of the available reactive sites on the surface and the steric hindrance due to the surface hydrogen, which enhances the reflection of the incoming radicals. These studies significantly improved our understanding of the growth of a-C:H films from CH_3 radicals. However, realistic a-C:H films differ from the studied model cases – well defined isolated dangling bonds on a diamond surface – in several respects. They have inherently rough surfaces and dangling bonds are present in a wide variety of atomic neighborhoods.

In this article we study the role of dangling bonds in the sticking of CH_3 radicals on realistic a-C:H surfaces using classical MD simulations. Surfaces with different sticking probabilities are created using the same instruments as in the particle beam experiments, namely atomic hydrogen exposure and ion bombardment. Identifying dangling bonds on these surfaces is by far not as straight forward as on well-defined diamond surfaces. We tackle this problem by potential energy analysis of the films using a hydrogen atom as a test particle and applying appropriate selection rules for dangling bond identification. Not all the identified dangling bonds show sticking, and the reactivity of those that do, has a large variation. By detailed characterization of the local environment we investigate what determines the reactivity of a dangling bond.

The article is organized as follows: the MD simulations and their results are discussed in Sections 2 and 3. The scheme to identify the active carbon atoms is presented in Section 4 and the discussion is in Section 5.

2. MD simulations

The simulations were carried out using the molecular dynamics code, HCParcas (Hydrocarbon Parallel Cascade) [42]. It uses a fifth-order predictor-corrected Gear algorithm to calculate the positions and velocities of particles using adaptive time-steps.

The Brenner potential was used to model C – C and C – H interactions [43–45]. The potential has been compared with tight binding, ab initio and DFT based calculations in the past by various authors [39,46–48]. These studies show that the Brenner potential is capable of describing short-range interactions accurately. It was shown by Sharma et al., that the Brenner potential can qualitatively describe the sticking of hydrocarbon radicals on a-C:H surfaces [36]. Träskelin et al. have compared the sticking of CH_3 radicals between the Brenner potential and a tight-binding approach based on a second order expansion of the Kohn–Sham total energy in density functional theory with respect to charge density fluctuations [39]. This study also shows that the sticking cross-sections have a qualitative match in both the cases. Hence, the computationally efficient classical Brenner potential appears adequate for the description of the present system.

The simulation has three parts: creation of an a-C:H film, preparation of different surfaces and bombardment with CH_3 radicals.

2.1. Sample generation

The a-C:H sample was created by repeated annealing and cooling of a random collection of carbon and hydrogen atoms. The details of sample preparation are described in [49]. Periodic boundary conditions were used along the X and Y directions and a free boundary was used along the Z direction.

The sample consists of 916 atoms (572 carbon atoms and 344 hydrogen atoms) and has a size of $1.4 \times 1.5 \times 2.7$ nm^3. The density is ~1.7 g cm^{-3} and the hydrogen content (H/(H + C)), is 0.375. For hydrocarbon films formed from ethane plasma discharges similar values of H content (0.39) and density (1.7 g cm^{-3}) have been reported [9]. The amorphous nature of the film was characterized by the radial distribution function (RDF) of the carbon atoms [49] and is in good agreement with the data obtained from neutron scattering experiments [50]. The numbers of three-fold and four-fold coordinated carbon atoms are 60% and 37%, respectively. This is in agreement with the properties of films which are intermediate between hard and soft [2]. Atoms within a distance of 0.3 nm of the bottom of the cell were fixed to mimic the effect of an underneath bulk layer. The fixed layer consisted of 64 carbon atoms and 36 hydrogen atoms. From now onwards these atoms are not included in computing any of the sample properties. Thus the number of carbon and hydrogen atoms that are used for computing the sample properties is 508 and 308, respectively. We call this the *virgin sample*.

2.2. Surface preparation

Three types of sample surfaces were created by bombarding the virgin sample by either hydrogen or argon atoms. Bombarding the virgin sample by one hundred hydrogen atoms of 0.5 eV energy results in an increase in the total number of hydrogen atoms of the sample from 308 to 316. Almost all of these hydrogen atoms were incorporated within a distance of 0.8 nm from the topmost atom location of the virgin sample. We call this *H-exposed sample*.

By continuing the hydrogen bombardment up to 500 H atoms, we created an *H-saturated sample*. The total number of H atoms increased to 329 and the added hydrogen distribution is limited to the top 0.8 nm which is similar to the H-exposed sample.

The *Ar-bombarded sample* was created by bombarding 14 Ar atoms of 100 eV energy on the virgin sample. The argon bombardment resulted in the sputtering of bound H atoms from the film within a distance of 1.2 nm from the topmost atom location of the virgin sample.

The properties of the samples are summarized in Table 1. The range of 100 eV Ar atoms within the sample is 1.2 nm and the damage creation and hydrogen elimination happened within this range [49]. Hence, the H content of this 1.2 nm thick surface region is calculated and is referred to as H_{top}.

Table 1
Properties of the samples. (H/(H + C)) is the hydrogen content of the complete sample (neglecting the atoms in the fixed layer at the bottom of the sample). The H content of the top 1.2 nm of the film is referred to as H_{top}.

Number	Sample	C	H	H/(H + C)	H_{top}
1	Virgin	508	308	0.377	0.39
2	H-exposed	508	316	0.383	0.41
3	H-saturated	508	329	0.393	0.45
4	Ar-bombarded	507	299	0.370	0.37