MODELING PECVD GROWTH OF NANOSTRUCTURED CARBON MATERIALS

E. Neyts¹, A. Bogaerts¹ and M. C. M. van de Sanden²
¹ University of Antwerp, Department of Chemistry, PLASMANT Research Group, Universiteitsplein 1, 2610 Antwerp, Belgium
² Eindhoven University of Technology, Department of Applied Physics, Den Dolech 2, 5600 MB Eindhoven, The Netherlands
E-mail: erik.neyts@ua.ac.be

ABSTRACT: We present here some of our modeling efforts for PECVD growth of nanostuctured carbon materials with focus on amorphous hydrogenated carbon. Experimental data from an expanding thermal plasma setup were used as input for the simulations. Attention was focused both on the film growth mechanism, as well as on the hydrocarbon reaction mechanisms during growth of the films. It is found that the reaction mechanisms and sticking coefficients are dependent on the specific surface sites, and the structural properties of the growth radicals. The film growth results are in correspondence with the experiment. Furthermore, it is found that thin a-C:H films can be densified using an additional H-flux towards the substrate.

KEY WORDS: molecular dynamics simulations, amorphous carbon, thin films, DLC, reaction mechanisms, growth mechanisms

1. INTRODUCTION

Carbon exists in a great variety of forms, ranging from various crystalline to amorphous structures, due to the different hybridizations it can exist in. Important carbon materials include crystalline diamond and graphite, in which the carbon atoms are sp³ hybridized and sp² hybridized, respectively. Furthermore, there are other carbon allotropes, including carbon nanotubes, fullerenes, polymers, and a broad class of amorphous materials, each having their own properties and technological importance. The amorphous materials can further be divided into those that consist of carbon only, and those that consist of carbon and one or several other materials, such as hydrogen, nitrogen, or metals. In the following, we will limit ourselves to amorphous carbon containing a certain fraction of hydrogen.

1.1. Structure and Growth Mechanisms

Based on their hydrogen content and properties, hydrogenated amorphous carbons (a-C:H) can be classified into four groups [1]:

1. a-C:H films with H-content of 40-50%. These films can have sp³ fractions
up to 60%. However, most of the sp\(^3\) bonds are H-terminated. Hence, there is no strongly interconnected sp\(^3\)-sp\(^3\) network, and these films are soft and porous. Usually, their hardness is below 10 GPa [2]. They are referred to as polymeric a-C:H (PLCH).

2. a-C:H films with intermediate H-content (20-40%). These films have generally lower sp\(^3\) content, but the C-C sp\(^3\) network is more extensive as compared to PLCH films. Hence, these films are denser and harder. Hardness values of up to 20 GPa can be obtained [2]. They are often referred to as diamond-like a-C:H (DLCH).

3. ta-C:H, or hydrogenated tetrahedral amorphous carbon. They contain up to 70% sp\(^3\) bonds, and a H-fraction of about 25%. These films have the highest density and hardness of all a-C:H’s, with a hardness of up to 50 GPa [3].

4. a-C:H with low H-content (< 20%). They have a high sp\(^2\) content, and are referred to as graphitic a-C:H, or GLCH. Their hardness is usually only a few GPa [4].

We use the term a-C:H is simply to denote a film composed of carbon and hydrogen, without any further specifications in terms of H-content or properties. Note that in the literature, the term DLC has often been used wrongly for this purpose.

Note that the categories as given above are not sharply defined. Furthermore, the overall structure is not necessarily homogeneous. For example, ta-C:H can locally contain crystalline fractions, embedded in a more amorphous matrix. DLCH can contain clusters of sp\(^2\) carbons, embedded in a sp\(^3\) matrix.

The growth mechanism of a-C:H films depend on the deposition technique used. When hard films are desired, the key property to aim for is a high sp\(^3\) fraction. Indeed, the sp\(^3\) matrix of hard DLCH and ta-C:H forms a rigid, strongly cross-linked network, determining the mechanical properties of the film. The deposition process which promotes sp\(^3\) bonding is ion bombardment [5-9]. The deposition mechanism of these hard films is currently understood in terms of the so-called “subplantation model”. Robertson proposed that the subplantation creates a metastable increase in density, leading to a local change in bonding to sp\(^3\) [10,11]. Various simulations demonstrated the basic idea of subplantation, see e.g. [12-15]. Carbon ions in the energy range of 10-1000 eV can penetrate up to a few nm into the growing film, loosing their energy mainly by elastic collisions with the target atoms (nuclear stopping). Hence, the carbon ions penetrate the surface, and enter a subsurface interstitial site. This increases the local density. The local binding will then reform around that atom according to this new density. The whole process consists of three stages: (a) a collisional stage (~ 0.1 ps); (b) a thermalization stage (~ 1 ps); (c) a relaxation stage (~ ns range). The thermalization and relaxation stages are presumed to allow the excess density to relax again, causing a loss of sp\(^3\) bonding at higher ion energies. At low ion energies, the increased sp\(^3\) content is explained by the increased penetration probability. At high ion energies, the decreased sp\(^3\) content is controlled by the relaxation. Although this model can explain the energy dependence of the sp\(^3\) fraction, the
relaxation stage of this process is not yet fully understood. Furthermore, the model cannot explain the transition temperature to sp² bonding at around 400-500 K, nor its dependence on the ion energy.

The deposition mechanisms are different in the softer a-C:(H) films. A schematic drawing is shown indicating various processes occurring at an a-C:H surface in Fig. 1. In the deposition of a-C:H films, the ion flux fraction is now much lower than 100%, and may be as low as only a few percents [2, 17]. Although the role of the ions remains the same as for the deposition of hard layers, i.e., increasing the sp³ fraction by the subplantation mechanism, the neutral species present in a PECVD setup will also contribute to the growth. Note that while subplantation is a physical process, while the chemisorption of neutrals is a chemical process. Indeed, the contribution of each neutral species to the growth rate depends on its sticking coefficient, which is in turn determined by its chemical surface reactivity [16].

Since the a-C:H surface is essentially fully covered by C-H bonds, it is chemically passive. Depending on their structure, different radicals will have different contributions. Diradicals, such as CH₂, can insert directly into C-C and C-H surface bonds. Hence, these species have sticking coefficients approaching 1. Closed shell neutrals, on the other hand, such as CH₄, have very low sticking coefficients and their effect is negligible. Monoradicals, such as CH₃, have a moderate effect. They can react with the film surface if dangling bonds are present, since they cannot insert directly into surface bonds. These dangling bonds can be created by removal of H-atoms at the surface. Hydrogen atoms can be removed either by an ion displacing the H-atom, or by an H-atom abstracting H from the C-H surface bond, or by an incoming radical such as CH₃. The latter mechanism is shown to be responsible for the synergistic effect of H on the sticking coefficient of CH₃ [18, 19].

![Diagram of deposition process]

**Fig. 1:** Schematic representation of the deposition process in a-C:H film growth: ion subplantation (1); surface dangling bond creation by ion impact (2); surface dangling bond creation by H-abstraction (3); addition of radical on surface dangling bond (4); H-abstraction from subsurface C-H bonds (5); H repassivating subsurface dangling bonds (6)
Neutral hydrocarbon radicals can only react at the surface, since they are too large to penetrate into the layer. Hydrogen atoms, on the other hand, can penetrate about 2 nm into the film [20], where they can create subsurface dangling bonds, abstracting H from subsurface C-H bonds. In this way, H₂ is formed, which can desorb from the film or become trapped interstitially. In sources where no substrate bias used, and ion bombardment of the substrate is negligible, growth proceeds entirely through chemical surface reactions.

1.2. Properties and Applications

The possible applications of the deposited film are dictated by its properties. The mechanical properties of a-C:H is of great importance because of their extensive use as protective coatings. Mechanical properties include e.g. hardness, density, adhesion, wear and friction. The hardness of a-C(:H) varies from very soft (a few GPa) to very hard (up to values of 88 GPa) [16], and is mainly determined by the sp³ fraction and the H-content. Closely related to the hardness is the density, varying between 1.2 g cm⁻³ for soft a-C:H films to 3.3 g cm⁻³ for superhard ta-C [7]. In order to ensure a proper adhesion of the carbon layer to the underlying substrate, deposition of one or several adhesion layers prior to the a-C:H film deposition, or ion beam mixing between the film and the substrate is usually performed [20, 21].

Amorphous carbon films are also notable for their low friction coefficients. For a-C:H, values as low as 0.01 [22] and 0.002 [23] have been reported. However, usually values between 0.02 and 0.15 are found for a-C:H. For comparison, the friction coefficient for steel on steel is about 0.8. These low friction coefficients are believed to be due to the hydrophobic nature of the surface. Indeed, contact with a different surface causes the formation of a transfer layer of a-C:H to be formed on the other surface. Thus, the contact is essentially between two hydrophobic a-C:H layers, which only interact with each other through van der Waals forces. The surface of ta-C on the other hand is believed to transform into graphitic layers upon contact and wear. These mechanisms also account for the resistance of these films to wear.

Furthermore, a-C:H films also show excellent chemical resistance. At room temperature, a-C:H films are chemically inert to practically any solvent, acid or base. Because of this chemical resistance and their continuity, a-C:H films can be used as corrosion-resistant coatings [19].

Thanks to these excellent mechanical, tribological and chemical properties, amorphous carbons are used in a variety of applications. As mentioned above, one of the main applications is their use as protective coatings, e.g. on magnetic hard discs. a-C:H is used because it can be made very thin, and it exhibits an extreme smoothness, it is continuous and chemically inert. Presently, there are no competitors as a coating material for this application. They are also used as protective coatings on e.g. razor blades, sunglasses [24] and bar-code scanners. This is possible due to the optical transparency of a-C:H in the IR region (apart
from the absorbing C-H bands). Furthermore, a-C:H can also be used as bio-
compatible coatings on parts such as hip joints, hart valves and stents, due to the
fact that the carbon material is biocompatible, has a low friction coefficient, and
does not produce metallic wear debris [25, 26]. Finally, a-C:H’s are also used in
electronic applications, although to a much lesser extent. One example is their
use as antifuses. An antifuse changes from high to low electrical resistance when
there passes a large current [27, 28].

1.3. Deposition Techniques

As mentioned above, various types of films can be deposited depending on the
type of deposition source used. The most popular techniques include ion beam
deposition (IB), sputtering and PECVD. The first DLC films were produced in
1971 by Aisenberg and Chabot using ion beam deposition [29]. In fact, ion beam
deposition is a term used to group several similar deposition techniques. The com-
mon feature of these techniques is to use a beam of carbon or hydrocarbon ions
with medium energy (tens to hundreds of eV). Typically, the ions are produced by
plasma sputtering of a graphitic cathode in an ion source [29, 30]. Alternatively,
a hydrocarbon gas can be ionized in a plasma [31, 32]. The ion beam can then be
extracted from the plasma source through a grid by a bias voltage. The ions are
accelerated in a high vacuum deposition chamber to form the actual ion beam.
Since the ion source runs at finite pressure, the beam also contains a fraction of
neutral species. Typically, ion beam deposition systems produce films that are
hard, dense and have a low surface roughness. Hence, films produced by these
sources are well suited for use as protective coatings.

The most common industrial deposition technique for amorphous carbons is
sputter deposition [33, 34]. The central idea is to sputter material from a graphite
electrode, which can deposit on the substrate. The sputtering is accomplished by
an Ar plasma, or, as in ion beam sputtering, by an Ar ion beam. A second Ar ion
beam can be used to bombard the growing film. This is called ion beam assisted
deposition [35]. Sputter sources generally have a rather low ion to neutral flux
ratio towards the substrate, such that very hard films cannot be produced in these
sources. On the other hand, these sources are very versatile and are easy to scale
up. Also, the deposition conditions can be controlled by the plasma power and the
pressure, and they are reasonably independent of the substrate geometry.

One of the most popular (laboratory) deposition techniques nowadays is radio
frequency PECVD [36, 37]. While in IB the substrate is placed in a deposition
chamber separated from the ion source, in PECVD the substrate is mounted on
one of the electrodes in the same reactor where the species are created. The reactor
consists of two electrodes of different area. The substrate is placed on the smaller
electrode, to which the power is capacitively coupled. Since the smaller electrode
acquires a larger bias voltage and becomes negative with respect to the larger
electrode, the negative sheath voltage at the smaller electrode will accelerate the
positive ions towards this electrode on which the substrate is mounted, promoting
the sp3 bonding. In order to maximize the ion to neutral ratio in the plasma, the plasma must be operated at the lowest possible pressure. Nevertheless, the ions are only about 10 percent of the film-forming flux even at pressures as low as 50 mTorr. Lower pressures cannot be used as the plasma will not longer strike.

A second disadvantage of this source is the energy spread in the ion energy distribution, prohibiting a controlled deposition. Yet another disadvantage of the rf PEVCD source is that it is not possible to have independent control over the ion energy and flux, as they both vary with the rf power. On the other hand, PECVD allows the deposition of uniform films over large areas, and PECVD systems can be easily scaled up. Films deposited by this source are generally medium hard, up to values of 30 GPa [38]. In order to overcome the disadvantages of rf PECVD, several similar techniques have been developed. Examples include microwave induced PECVD, allowing for a lower gas pressure and a higher ion to neutral ratio [39], and electron cyclotron resonance microwave plasma CVD (ECR-MPCVD). The latter technique also allows for a higher plasma density, and control over the ion energy separately from the ion flux [40-42].

Finally, another variant of the PECVD technique is the expanding thermal plasma (ETP). The ETP is a remote source, consisting of two parts: a cascaded arc in which the plasma is created, and a reactor chamber, in which the substrate is placed [43]. A schematic drawing of the set-up is shown in Fig. 2.

![Fig. 2: Schematic drawing of the ETP set-up](image_url)

An Ar thermal plasma is created in the cascaded arc plasma source, operated at sub-atmospheric pressure. The argon plasma expands into the low pressure reaction vessel. At the top of the reaction vessel an injection ring is placed. The hydrocarbon gas is admixed into the emanating plasma by means of this injection ring. In the expanding plasma, many chemical reactions take place, and the
growth species are created. These species subsequently reach the substrate where they can deposit.

In [44-50], the ETP source was used with acetylene as the hydrocarbon gas. Since no substrate bias was applied, ion bombardment of the substrate is precluded. Nevertheless, medium hard films could be obtained with a hardness of 14 GPa, Young’s modulus of 120 GPa, a refractive index of 2.2 and a density of 1.7 g.cm$^3$. Furthermore, the films showed good adhesion on glass and crystalline silicon, as well as chemical stability. The main advantage of this technique, however, is the ultra-high deposition rate of 70 nm.s$^{-1}$. It has also been shown that the film quality is improved under high deposition rate conditions [45, 46]. Several studies have been carried out to elucidate the plasma chemistry and the growth species generation [46-50]. It was determined that the crucial factors determining the film properties, as well as the growth rate, were the arc current and the acetylene loading. The type of growth species that are created in the expanding plasma, is determined by the ratio between the fluxes of the acetylene and the Ar$^+$ ions:

$$F = \frac{\Phi_{C_2H_2}}{\Phi_{Ar^+}}$$

When the C$_2$H$_2$ flow is smaller than the argon ion and electron fluencies emanating from the plasma source, i.e., F < 1, the acetylene is fully decomposed by the plasma reactions, leading to the formation of C, CH, CH$_2$, C$_2$ and C$_2$H. C and C$_2$ radicals have the highest densities, and are presumed to be responsible for the growth of soft, polymer-like a-C:H films formed under these conditions [47].

When the acetylene flow is higher than the argon ion and electron fluencies emanating from the plasma source, i.e., F > 1, the acetylene is only partially decomposed into C, CH, CH$_2$, C$_2$ and C$_2$H. Under these conditions, the C$_2$ and C$_2$H radicals can react with the remaining C$_2$H$_2$ leading to the formation of C$_4$, C$_3$H and C$_4$H$_2$. The C and CH radicals on the other hand react with C$_2$H$_2$ leading to the formation of mainly C$_3$ and C$_3$H. These species are unreactive in the gas phase. It was shown that the C$_3$ radical has the highest density in the region close to the substrate, and its density was correlated with the measured growth rate. Since its surface reactivity was previously already reported to be high [51], it was suggested that the C$_3$ radical is probably responsible for the fast growth of hard a-C:H films under F > 1 conditions. However, it was also found that the stoichiometry of the film could not be explained by the carbon containing growth species alone. Hence, it was concluded that additional hydrogen has to be incorporated into the film during the growth.

Although most of the plasma chemistry in the ETP was elucidated, and the important (presumed) growth species have been identified, the actual growth process remains unclear. More specifically, questions remain regarding the actual growth mechanism, the surface reactions, and the role of the additional hydrogen during film growth. In this paper, we have investigated the above mentioned growth mechanisms and film growth by means of molecular dynamics (MD) computer simulations. In the following section, the simulation model will be described. In
section 3, the results will be presented for the simulated film growth under $F < 1$
conditions. Finally, a conclusion will be given.

2. DESCRIPTION OF THE SIMULATION MODEL

In this study, a classical molecular dynamics (MD) model is used. The original
code was developed by Tanaka et al. [52], and subsequently modified. The inter-
atomic potential used in these simulations is the well known Brenner potential for
hydrocarbons [53]. In the MD methodology, the atoms in the system are followed
through space and time by integrating Newton's law. The atoms move under the
influence of forces derived from the interatomic potential. The integration scheme
used is the velocity-Verlet algorithm [54]. The time step used is invariably set to
0.2 fs, ensuring energy conservation to at least $2 \times 10^{-49}$.

The growth species included in the simulation were based on experimental
measurements during the ETP deposition of a-C:H films. These species and their
relative fluxes are given in Table 1. Since the flux of hydrogen towards the substrate
could not be measured experimentally, a relative H-flux ($\Phi_{H, \text{rel}}$) was used in the
range between 0 and 45%. The kinetic energy of the impacting species was set to
0.13 eV. In these growth simulations, a clean diamond \{111\} surface is exposed
to normal particle impacts.

**TABLE 1: Growth Species and Their Fluxes**

<table>
<thead>
<tr>
<th>Species</th>
<th>Relative flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.71(1-$\Phi_{H, \text{rel}}$)</td>
</tr>
<tr>
<td>CH</td>
<td>0.05(1-$\Phi_{H, \text{rel}}$)</td>
</tr>
<tr>
<td>C₂</td>
<td>0.20(1-$\Phi_{H, \text{rel}}$)</td>
</tr>
<tr>
<td>C₂H</td>
<td>0.04(1-$\Phi_{H, \text{rel}}$)</td>
</tr>
<tr>
<td>H</td>
<td>$\Phi_{H, \text{rel}}$</td>
</tr>
</tbody>
</table>

Each impact was followed for 2 ps, applying a Berendsen heat bath set at
100 K during the last 0.4 ps [55]. The films are grown by consecutive particle
impacts, i.e., the output of every impact is the input for the next impact. After
each impact, unbound atoms and molecules are removed from the configuration
based on 1st order desorption theory. Growth was continued until the films reached
a thickness of about 10 nm, each containing about 4000 atoms. After the growth
phase, the films were allowed to relax for another 10 ps, after which the final
data was collected.

Although we have previously applied this model successfully to study the deposi-
tion of thin a-C:H films and the reaction mechanisms of hydrocarbon radicals (see
e.g. [56-59]), the model also has several shortcomings. First, surface diffusion of
atoms is currently not yet taken into account. As a result of this, the deposition rate in the simulation is orders of magnitude higher compared to the experiment, since the time between impacts – during which diffusion could occur – is ignored in the simulation. Second, the Brenner potential as used in this work does not take into account intermolecular forces. Third, the kinetic energy of the impinging particles is very low, requiring a long simulation time to allow for sufficient relaxation of the resulting structure. This is partially accounted for by using the heat dissipation bath after each impact. Finally, it should also be noted that the reaction mechanisms determined by classical MD are very sensitive to the exact potential energy surface used, possibly requiring a potential more accurate than the Brenner potential.

3. THIN A-C:H FILM GROWTH FROM LOW KINETIC ENERGY HYDROCARBON RADICALS

Using the model as described above, the growth of thin a-C:H films were simulated using the species from Table 1. More information regarding these simulations can be found in [56].

In Fig. 3a, the calculated evolution of the H-content in the deposited films is shown as a function of the H-flux towards the substrate during growth. From the figure it can be seen that the uptake of hydrogen is nearly a linear function of the H-flux. This H-uptake in the films determines the fractions of CH\textsubscript{x} fragments in the films, as shown in Fig. 3b. Note that the formation of bulky CH\textsubscript{2} groups only occurs at a H-content in the film of about 25% or more. Even at the highest H-fluxes studied in the current work, the fraction of CH\textsubscript{3} groups in the films remained negligible. It can therefore be concluded that in these films, the hydrogen is not chain terminating. The H-uptake in the film and the concurrent formation of the CH\textsubscript{x} fragments induces an increase in the mass density and atom density as described below.

![Graphs](image)

**Fig. 3:** (a) Calculated H-content as a function of the H-flux towards the substrate. (b) Calculated fraction of CH\textsubscript{x} fragments as a function of the H-content.
Previously, Ferrari et al. have already shown the decrease in mass density of a-C:H films with increasing H-content for films containing more than 40% sp³ content (see [60] and references therein). In Fig. 4, it is shown that this effect also occurs under the conditions used in this study for high enough H-fluxes. The figure shows the calculated evolution of the mass density and atom density of the different films as a function of the H-content in the bulk of the films.

Different stages (in terms of the H-flux towards the films or H-content in the films) can be seen. At low H-fluxes, little H is present in the film, and the mass density increases as a function of the H-content, until a maximum is found at a H-content of about 10%. The atom density, on the other hand, continues to increase as a function of the H-content. Indeed, a high H-flux allows the incorporation of a large H-fraction into the carbon matrix, increasing the atom density. This, however, does not increase the mass density due to the low H mass.

As can be seen in Fig. 4, a maximum in the atom density is found at a H-content of about 22%, corresponding to a H-flux towards the substrate of about 30% (see Fig. 7). The occurrence of the bulky CH₂ groups at high H-fluxes (see Fig. 3b) accounts for the decrease in both the mass density and atom density at a H-content > 25%. Also, as more H is incorporated in the film, relatively less C atoms must accommodate relatively more H-atoms, increasing the average carbon coordination number, in the range of 2.8-3.1 for a H-flux varying between 0% and 45%.

The observed increase in mass density with increasing H-content at low H-fluxes can be explained by the changing hybridization state of the carbon matrix. Indeed, the uptake of H into the films also considerably changes the microstructure of the films. In Fig. 5, the evolution of the sp, sp² and sp³ C-sites in the bulk of the film is shown as a function of the H-content. Here, one- or two-coordinated carbon atoms are identified with sp hybridized C-atoms. Similarly, sp² and sp³ carbon atoms are identified as three-coordinated and four-coordinated carbon atoms, respectively. It can be seen in the figure that increasing the H-content in the film decreases the
**Fig. 5:** Calculated sp, sp$^2$ and sp$^3$ fractions in the films as a function of the H-content. Note how the sp$^2$ fraction first increases, then remains constant, and finally decreases as the H content in the film increases.

sp content, and increases the sp$^2$ content. This transition of sp to sp$^2$ bonding as a function of the H-content coincides with the increase in mass density at low H-fluxes. In this region, the film structure is composed of a network of sp$^2$-like C-C bonds, stabilized by chemical resonance. Since sp sites occupy a larger volume per atom than the sp$^2$ sites (sp sites are linear, one-dimensional structures while sp$^2$ sites are two-dimensional), the sp to sp$^2$ transition effectively lowers the volume occupied in the film per atom, and hence increases the mass density.

Higher H-fluxes further lower the sp content and strongly increase the sp$^3$ content due to the increasing CH and CH$_2$ fractions, whereas the sp$^2$ content remains more or less constant. In this region, a considerable fraction of the film volume is taken by the H-atoms, contributing only to the atom density, and hardly to the mass density. Hence, the films now become more porous and less dense.

At even higher H-fluxes ($\Phi_{\text{H}} > 0.30$), the sp$^2$ carbon atoms are converted into sp$^3$ carbons, coinciding with the maximum in the atom density. As mentioned above and as can be seen in Fig. 3b, the fraction of bulky CH$_2$ groups now becomes important. These groups repel each other, such that from this point on, both the atom density and the mass density decrease. Hence, as the H-flux towards the substrate increases, there is a H-induced sp to sp$^2$ to sp$^3$ shift.

As mentioned before, the H-flux towards the substrate could not be determined experimentally. From these simulations, however, an estimate can be made. The films deposited experimentally under conditions corresponding to the current simulation, show a H-content of about 33%, and a mass density of about 1.5
g.cm-3. As can be seen from Fig. 4, this experimental result is reproduced by our simulations.

4. CONCLUSIONS

Plasma Enhanced Chemical Vapor Deposition (PECVD) has become one of the preferred methods to deposit nanostructured carbon materials. Because of the complex nature of the deposition process, simulation tools such as Molecular Dynamics have become invaluable in deepening our understanding of the underlying processes. In this paper, we have exemplified this by studying in detail the deposition process of amorphous hydrogenated carbon (a-C:H) films by PECVD. These a-C:H films (can) have excellent mechanical, tribological and chemical properties, rendering them important technological materials that are used in various applications.

Thin a-C:H film growth was simulated, corresponding to expanding thermal plasma conditions. Species were chosen on the basis of experimental measurements. Good correspondence was found for deposition from low acetylene fluxes as hydrocarbon source. Furthermore, it is shown how low hydrogen fluxes towards the substrate can induce a microstructural change in the film, leading to an increase in the mass density and atom density of the film. Higher H-fluxes result in a decrease of the mass and atom density of the film. Finally, also the H-flux towards the substrate that could not be measured experimentally, can be obtained from the simulation results.

ACKNOWLEDGMENTS

One of the authors (E. Neyts) is indebted to the FWO-Flanders for financial support. The authors would also like to thank J. Benedikt for the many fruitful discussions on the chemistry in the expanding thermal plasma and the deposition mechanisms.

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