

# Atomistic simulation of the bombardment process during the BEN phase of chemical vapor deposition (CVD) of diamond

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## Abstract

We present the results of the first molecular dynamics simulations under realistic conditions pertinent to the incubation period of the bias enhanced nucleation process of diamond, based on the experimentally obtained average energies of CH<sub>3</sub> and C<sub>2</sub>H<sub>2</sub>, at different bias voltages. It was found that the energies measured at a bias where the nucleation enhancement sets in are critical for the subplantation of both types of ions. In the case of the typically applied bias voltages, acetylene plays the dominant role. The molecule breaks up and the average final penetration depth of the carbon atoms is ~5 Å. The bombardment causes a significant increase of the mass density and the sp<sup>3</sup> content in the range 4–8 Å below the surface despite the elevated temperature. The depth obtained for the main structural changes agrees well with the width of the amorphous carbon layer observed at the end of the incubation period for epitaxial nucleation. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Computer simulation; Nucleation; Ion bombardment; Carbon vapor deposition (CVD)

## 1. Introduction

The bias enhanced nucleation (BEN) process [1–3] is frequently used to achieve higher nucleation density in the chemical vapor deposition (CVD) of diamond layers. In the BEN process the hydrocarbon content of the gas (2–10%) would lead to the growth of an amorphous hydrogenated carbon (a-C:H) layer. However, after a given incubation period, diamond nuclei appear as a result of the ion bombardment due to the negative bias (–200 V) applied to the substrate. The most abundant ionic species striking the surface and their energy distributions have been determined recently by Kátai et al. [4–6] using in-situ ion-beam mass spectrometry (IBMS) in the BEN phase of microwave plasma CVD of diamond. The measurement of average ion energies as a function of the bias voltage up to 200 V showed a linear relationship for all species except for CH<sub>3</sub> and CH<sub>4</sub>, for which the average energy saturated at approximately 30–40 eV [4]. At 200-V bias and 4% CH<sub>4</sub> in the gas flow, approximately 85% of the total

hydrocarbon flux is determined by six species, C<sup>+</sup>, CH<sup>+</sup>, CH<sub>2</sub><sup>+</sup>, CH<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>2</sub><sup>+</sup> and C<sub>2</sub>H<sub>3</sub><sup>+</sup>, with average kinetic energies between 40 and 80 eV. These experiments seem to support the application of the subplantation model for explaining the mechanism underlying the BEN process [7–10]. The subplantation model was originally developed to describe the dependence of the sp<sup>3</sup>-bonded carbon content on the energy of bombarding ions in the low temperature ion beam synthesis of tetrahedral amorphous carbon (ta-C) [11,12]. An energy window exists in which the ions have sufficient energy to penetrate below the surface of the growing a-C layer, but not so high as to cause thermal spikes which would allow the system to relax the stress built up by the increase of density due to these ions. The accumulating stress causes local sp<sup>2</sup> to sp<sup>3</sup> conversion [13]. In the case of the BEN of diamond CVD the situation is different. First of all, instead of single monoenergetic species, a number of different molecular ions strike the surface with different energies. Secondly, there is an abundance of hydrogen and the growing layer is a-C:H, instead of a-C. Finally, the substrate is heated to 700–900 °C, which was assumed to preclude the sustenance of sp<sup>3</sup>-bonding leading to nanocrystalline graphitic car-

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bon formation instead [7]. Therefore, in the subplantation model applied to BEN in diamond CVD [7], the effect of the stress was assumed to cause an ordering of graphitic platelets perpendicular to the substrate surface to which they are bonded, and diamond nucleation was assumed at the edge of these platelets according to the model of Lambrecht et al. [14]. This speculative model of BEN can also explain the epitaxial orientation of diamond nuclei under specific conditions.

It is very difficult to obtain direct experimental evidence on the correctness of such models, although the graphitic intermediate layer with basal planes oriented perpendicular to a Si surface seem to have been observed [15]. Molecular dynamics (MD) simulations can, however, shed light on the details of the nucleation process. So far, only the ion beam synthesis of ta-C could be examined, where the bombarding ion ( $C^+$ ) and its energy has been known. Uhlmann et al. [16] performed MD simulations to study the penetration of carbon atoms into a ta-C film at different energies. It was shown for kinetic energies higher than 30 eV that the carbon atoms penetrate and occupy subsurface positions. The average penetration depths were  $\sim 2$  Å at 20 eV,  $\sim 3$  Å at 40 eV, and  $\sim 5$  Å at 80 eV. The evolving layer had a defective, low-density  $sp^2$ -rich surface layer, below which a dense  $sp^3$ -rich layer was developing.

In this paper we will report on quantum mechanical MD simulations performed under realistic conditions corresponding to BEN in diamond CVD. A heated a-C:H layer is bombarded with methyl and acetylene ions of different energy in the range measured in Kátai et al. [5]. We concentrated on the incubation period of nucleation, studying the penetration characteristics and possible break-up of hydrocarbon ion species as well as the structural changes in the target substrate.

## 2. Details of the simulation

The non-orthogonal, density-functional based tight binding method (DFTB) [17,18] used in this paper for MD simulations, is identical with that in Uhlmann et al. [16]. The net CPU (central processing unit) time used for the simulations was approximately 15 weeks on DEC-ALPHA workstations.

### 2.1. Generation of the a-C:H target

The a-C:H layer was generated from a three-dimensional periodic, cubic supercell with edges of 10.66 Å. The structure of the supercell was obtained by cooling a random distribution of 128 carbon and 69 hydrogen atoms from 8000 K to room temperature over 8 ps. The mass density in this supercell was 2.2 g/cm<sup>3</sup>, and the average first neighbor co-ordination number was 2.88. First, we doubled the supercell in one direction, which we refer to as the  $z$ -axis in the following. Then the

periodic boundary condition along this axis was broken. To economize on computer resources, we cut away the bottom part of the layer 15 Å below the top surface. The broken  $\sigma$ -bonds at the bottom were saturated by hydrogen atoms. The other surface was chosen to be exposed to bombardment. To minimize the energy of the layer obtained this way, an annealing at 2000 K was carried out for approximately 1 ps, with a time step,  $\Delta t = 41$  a.u. ( $\sim 1.0$  fs). This equilibrated structure was subsequently cooled down to 30 K within approximately 1 ps, and was then allowed to relax using a conjugate gradient method. Finally, this low energy structure was annealed at 1000 K for approximately 1 ps to prepare the substrate for bombardment at the temperature used in BEN.

The target created this way contained 182 carbon and 107 hydrogen atoms, 16 of the latter terminating the broken  $\sigma$ -bonds at the bottom. The average mass density was 1.98 g/cm<sup>3</sup>. In the simulation of the bombardment we allowed the 190 atoms in the top 11.1-Å-thick part of the target to move freely. The rest of the slab at the bottom with a thickness of 4 Å, was kept fixed in all simulations. In the following we will define the range within 3 Å from the atom with the highest  $z$ -coordinate as the ‘surface layer’ of the target, while the rest will be called the ‘bulk’ (see Fig. 1). The average mass density of the bulk was  $\rho^{\text{bulk}} = 2.05$  g/cm<sup>3</sup>. The target contained 6.6, 48.4, 5.5 and 38.5% of  $sp^1$ ,  $sp^2$ ,  $sp^{(2+x)}$  and  $sp^3$  bonded carbon atoms<sup>1</sup>, respectively. The mass density profile in Fig. 1 shows that there is no significant deviation from the average density in the ‘bulk’.

### 2.2. Bombardment by $C_xH_y$ projectiles

Among the many  $C_xH_y$  hydrocarbon species striking the surface during BEN, we selected methyl,  $CH_3^+$ , and acetylene,  $C_2H_2^+$ . Experiments showed [4,5] that the flux of species with  $x > 2$  is negligible. Among the  $x = 2$  species  $C_2H_2$  has the highest total flux, 2–3 times higher than any other hydrocarbon or carbon ion. Within the group of  $x = 1$ ,  $CH_3$  is not dominant but it is thought to be a key player in diamond growth. Also, its behavior with respect to increasing the bias is unique, its average energy saturates at approximately 40 eV [4]. Accordingly, bombardment with energies of 20 and 40 eV was simulated in the case of methyl, while 20, 40 and 80 eV was used in the case of acetylene to study the energy dependence of ion bombardment. The 20-eV value was chosen to represent the effect of bias voltages below the limit of nucleation enhancement [4]. Approximately 40 eV is the maximum energy of methyl ions and the typical energy of acetylene ions around the critical

<sup>1</sup> The notation  $sp^{(2+x)}$  refers to a carbon atom with three neighbors, but in an environment and bonding state corresponding to  $sp^3$  hybridization. In short, having a ‘dangling bond’ in the fourth direction.

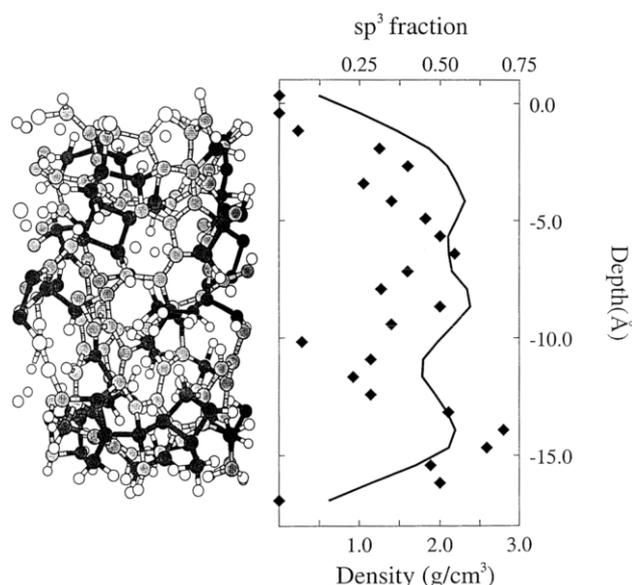


Fig. 1. The target structure and its  $sp^3$ -fraction and mass density profile. The black, gray and light-gray circles are carbon atoms with coordination  $Z=4, 3$  and  $\leq 2$ , respectively. White circles denote hydrogen atoms. (For a color version see <http://www.physik.uni-marburg.de/~kohary/CxHybomb.html>.) The solid line in the plot on the right shows the mass density and the diamonds show the  $sp^3$ -fraction.

voltage [4]. The 80-eV value was chosen to represent the effect of bias at 200 V and above.

The bombardment was simulated as follows. In the first, collision stage, which describes the penetration and the energy loss of the species, a projectile with given kinetic energy was directed towards the target. The starting lateral position of the projectile with respect to the surface was selected randomly. The atom of the projectile closest to the surface was always placed 4 Å over the surface. We considered two different orientations for both species. For  $C_2H_2$  the molecular axis is either aligned with the  $z$ -axis, or perpendicular to that. In the case of  $CH_3$ , the alignment of the plane of the methyl radical is either perpendicular to  $z$  or parallel to it. These orientations represent extreme cases embracing the various possibilities. A random variation of the orientation with suitable statistics would have required too much computation. Instead, we chose to average the results over these extremes. Starting with the given kinetic energy of the projectile, the collision stage was simulated for 7500 a.u. ( $\sim 182$  fs). During this period the kinetic energy of the substrate was rescaled to 1000 K by the velocity rescaling method, keeping the target at a constant temperature. For different starting kinetic energies different time steps were used;  $\Delta t=15, 10$  and 5 a.u. for  $E_{kin}=20, 40$  and 80 eV, respectively. In the *thermalization stage*, when the local structure relaxes dissipating the ion energy into the lattice, and the projectile atoms become part of the substrate, their

velocities were also rescaled for approximately 0.5 ps ( $\Delta t \sim 0.5$  fs) to keep the substrate temperature at 1000 K. The next projectile was started over this relaxed substrate. Altogether, ten projectiles were shot in (in the case of each orientation and each energy). This means approximately a dose of  $10^{15} \text{ cm}^{-2}$ , corresponding to that arriving in  $\sim 1$  s of real-life BEN. We note here that some projectile atoms were scattered back and some hydrogen atoms were sputtered out from the film.

### 3. Results

#### 3.1. Penetration of the projectiles

In our simulations 10 Å was found to be the deepest penetration into the target (with respect to the original surface). This shows that our choice of 11 Å as the relaxing part of the film was reasonable. The average of the maximum and final penetration depths are shown in Table 1. The results do not differ much from those obtained in Uhlmann et al. [16]. For subcritical energy (20 eV), the projectile ions end up in the surface region. At the critical 40-eV kinetic energy the final penetration depth, averaged over orientations, is just beyond the boundary of the ‘surface’ and ‘bulk’ region of the target in case of both species. Since approximately 30–40 eV have been measured for both species at the bias voltage where nucleation enhancement starts, these results show that the BEN is definitely a subplantation process. Acetylene ions with kinetic energy of 80 eV penetrate to approximately 5–6 Å.

#### 3.2. Dissociation of the projectiles

Dissociation of the molecular ions depends on their kinetic energy (see Table 2). For acetylene the carbon–carbon bond was almost never broken at low energies. At high bombarding energies (80 eV), the carbon–carbon bond was broken in 70% on average. The number of broken C–H bonds increases continuously with the bombarding energy, reaching 85% at 80 eV in the case of acetylene but being above 60% even at 40 eV for both projectiles. It has to be noted that at 40 eV both

Table 1

The average maximal penetration depths of the projectile carbon atoms

$E$ (eV)	$C_2H_2$ ; $C_1$ (Å)	$C_2H_2$ ; $C_2$ (Å)	$CH_3$ ; C (Å)
20	–2.56 (–2.04)	–2.73 (–1.90)	–2.79 (–1.95)
40	–3.80 (–3.49)	–3.81 (–3.79)	–3.68 (–3.06)
80	–6.04 (–5.81)	–5.26 (–4.78)	– (–)

The average final penetration depths are given in brackets. For the latter case only projectile atoms ending up under the original surface were considered.

projectiles usually retain one hydrogen atom bonded to carbon. Regarding the experimental observation that at usual bias voltages (at and above 200 V) methyl ions have an energy of  $\sim 40$  eV and acetylene ions approximately 80 eV; these results imply that irrespective of the incoming species, the implanted particles are typi-

cally C and CH radicals and some  $C_2$ . The analysis of the final configuration of the implanted carbon atoms in the film show that they mostly end up in an  $sp^{(1+x)}$  and  $sp^2$  hybridization state. The excess hydrogen tends to form  $H_2$  molecules.

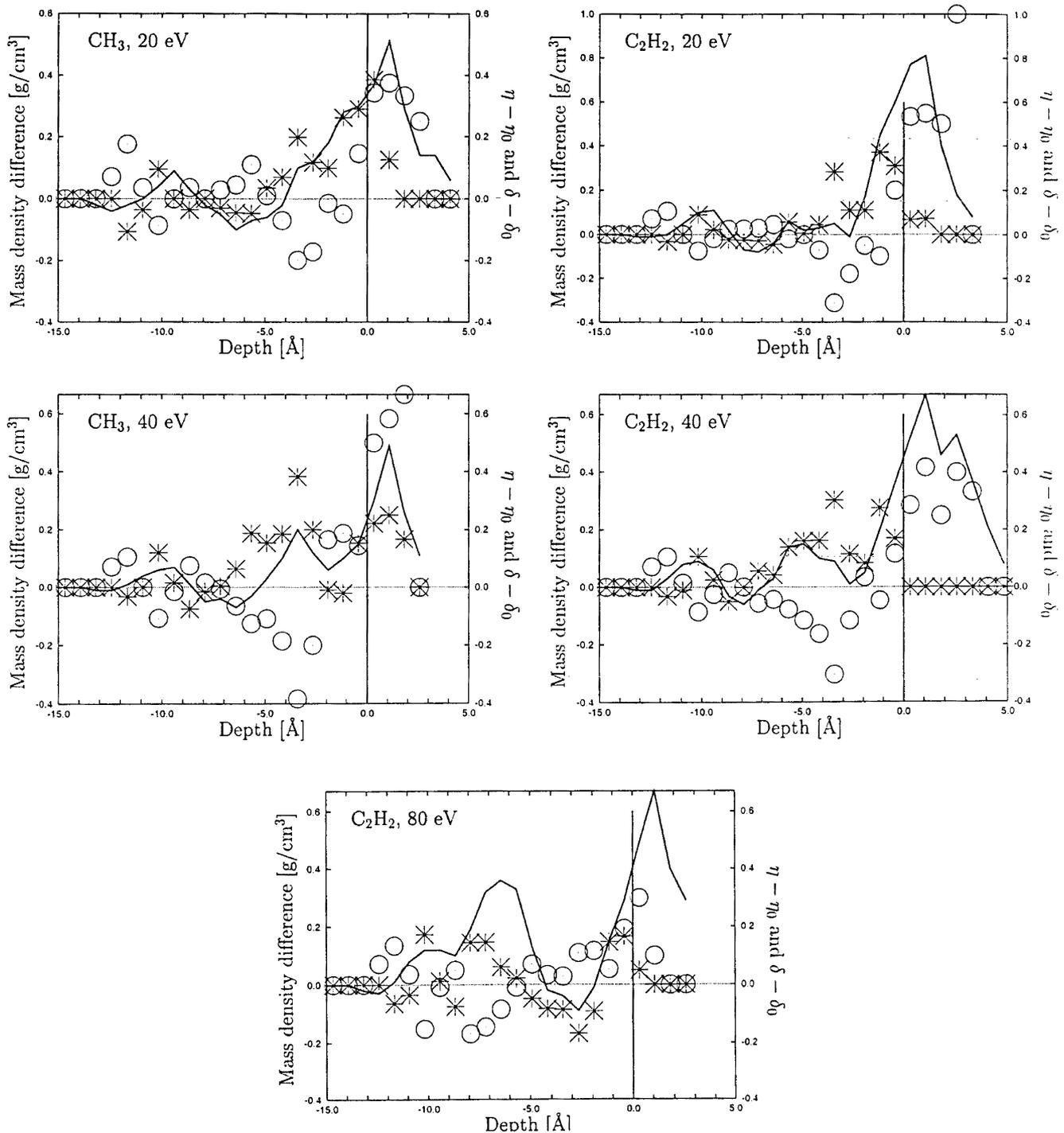


Fig. 2. Depth profiles of a-C:H targets after 10 collision events (averaged over orientation). Solid lines show the difference in the mass density distribution between the final and the initial structures. Circles and stars denote the differences in the  $sp^2$  ( $\eta - \eta_0$ ) and  $sp^3$  ( $\delta - \delta_0$ ) fractions, respectively. Vertical straight lines indicate the position of the original surface of the starting target.

Table 2  
Average number of bonds broken in 10 projectiles

E (eV)	C <sub>2</sub> H <sub>2</sub>			CH <sub>3</sub>		
	H <sub>1</sub> –C <sub>1</sub>	C <sub>1</sub> –C <sub>2</sub>	C <sub>2</sub> –H <sub>2</sub>	C–H <sub>1</sub>	C–H <sub>2</sub>	C–H <sub>3</sub>
20	2.0	0.0	3.0	4.0	5.0	5.0
40	6.0	1.0	8.0	7.5	8.0	8.5
80	8.5	7.0	9.0	–	–	–

### 3.3. Structural rearrangement

The bombardment of the projectile atoms caused structural rearrangement in the substrate. The thickness of the target grew by 1–3 Å after 10 subsequent bombardments. The total sp<sup>3</sup> content in the film increased by 1–5%, while the total sp<sup>2</sup> content decreased by the same magnitude (in contrast to the assumption in Robertson et al. [7]). After only ten projectiles, there is no significant change in the average mass density or in the average first neighbor distances. No formation of diamond nuclei have been observed.

In Fig. 2 the mass density and the sp<sup>2</sup>, sp<sup>3</sup> fraction differences between the final and the initial target are shown as a function of depth for all cases. At 20 eV, structural rearrangement can only be observed in the ‘surface’ region to within approximately 3.0 Å from the original top of the substrate. The sp<sup>3</sup> content increases by 20–30% and the sp<sup>2</sup> content decreases by the same magnitude. For 40 eV there are significant changes in a deeper region between –6.0 and –3.0 Å, again increasing the sp<sup>3</sup> content at the expense of the sp<sup>2</sup> but in a broader range. There is no significant difference between the effect of the two different projectiles. For C<sub>2</sub>H<sub>2</sub> bombardment with 80 eV, significant changes can be seen in the target structure down to –10.0 Å. The increase of the sp<sup>3</sup> content occurs in the –5.0 to –10.0 Å range. In all cases, the structural rearrangement is accompanied by a change in mass density, the latter growing with sp<sup>3</sup> content. This effect is most significant at 80 eV. The strongest increase in mass density occurs in the –4 to –8 Å region. (Note that the mass density increase over the top of the initial surface comes from the slow growth of the layer.) It is interesting to note that the effect of the 80-eV acetylene ions is markedly different from that of the 40-eV methyl ions, despite of the fact that the C–C bond breaks up in the former and the energy per carbon atom is approximately the same as in the case of the latter. For the typically applied bias voltage, methyl ions with 40 eV and acetylene ions with 80 eV energy are relevant. It can be seen that the effect of acetylene is dominant.

### 4. Conclusions

We have presented the results of the first MD simulation under realistic BEN conditions, based on the

experimentally obtained average energies of the ionic species, CH<sub>3</sub><sup>+</sup> and C<sub>2</sub>H<sub>2</sub><sup>+</sup>, at different bias voltages. The a-C:H target with an average mass density of 1.98 g/cm<sup>3</sup> was kept at 1000 K, typical for BEN. Our findings show that the processes occurring during BEN in the target are very similar in effect to those in the low temperature ion beam synthesis of ta-C layers, despite the differences in the projectiles, in substrate temperature and the presence of hydrogen. The sp<sup>3</sup> content increases and is sustained in this case, too. Acetylene ions play the dominant role although they break up in course of the bombardment process. No formation of diamond nuclei or aligned graphitic planes has been observed, although the relatively small number of implanted atoms can be the reason for that.

In recent experiments [6] an X-ray photoelectron spectroscopic (XPS) study of the surface composition of films nucleated under different conditions have been carried out. Comparing samples where the nucleation was terminated within or beyond the time window where heteroepitaxial nucleation occurs, it was found that in the former case the thickness of the a-C:H layer grown in the incubation phase varied between 5 and 8 Å (depending on the methane content of the feed gas) while it was between 12 and 17 Å, for the latter. Taking into account the results of our simulation — showing that the main ionic species cause density increase and thereby stress in a region 4–8 Å below the surface of the a-C:H layer — this implies that nucleation occurs at the substrate surface which must have a role in the formation of the nuclei, as assumed in Robertson et al. [7]. Simulation of the bombardment of an a-C:H layer of such thickness on top of a Si surface is under way. At the same time, it should be noted that non-epitaxial nucleation must commence via a different mechanism. The simulation of that process requires a substantial increase in the investigated dose and therefore, in computer time.

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