# Modeling adatom surface processes during crystal growth: A new implementation of the Metropolis Monte Carlo algorithm

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In this paper, a new implementation of the Metropolis Monte Carlo (MMC) algorithm is presented. When combining the MMC model with a molecular dynamics (MD) code, crystal growth by plasmaenhanced chemical vapor deposition can be simulated. As the MD part simulates impacts of growth species onto the surface on a time scale of picoseconds, the MMC algorithm simulates the slower adatom surface processes. The implementation includes a criterion for the selection of atoms that are allowed to be displaced during the simulation, and a criterion of after how many MMC cycles the simulation is stopped. We performed combined MD-MMC simulations for hydrocarbon species that are important for the growth of ultrananocrystalline diamond (UNCD) films at partially hydrogenated diamond surfaces, since this implementation is part of a study of the growth mechanisms of (ultra)nanocrystalline diamond films. Exemplary for adatom arrangements during the growth of UNCD, the adatom surface behavior of C and  $C_2H_2$  at diamond (111)1 × 1, C and  $C_4H_2$  at diamond (111)1 × 1 and  $C_3$  at diamond (100)2 × 1 has been investigated. For all cases, the diamond crystal structure is pursued under the influence of MMC simulation. Additional longer time-scale MD simulations put forward very similar structures, verifying the MMC algorithm. Nevertheless, the MMC

### 1. Introduction

In surface science, many physical phenomena are dynamic in nature. For theoretical investigations of thin film growth (including chemisorption and desorption of atoms), the dynamics of the system should be taken into account. Therefore, molecular dynamics (MD) simulations are a very powerful tool for the study of crystal growth on atomic level.<sup>1</sup> In MD simulations, the atoms of the considered system interact through a potential function, based on Newtonian dynamics.<sup>2</sup> The positions and velocities of the atoms are calculated for each discrete time step during the simulation by integrating the equations of motion. The chosen time step must be short compared to the vibrational frequencies of the atoms, *i.e.*, in the order of femtoseconds. Hence, to assure a reasonable calculation time, the total simulated time, *i.e.*, the sum of all simulated time steps, is only in the order of picoseconds. At maximum, the range of MD simulations reaches the time scale of nanoseconds.

However, a number of processes that are relevant for the evolution of thin film growth, *e.g.* relaxation processes and diffusive events, take place at the microsecond time-scale.<sup>3</sup> Consequently, those processes cannot be simulated by means of MD.

In order to simulate the whole deposition process of thin film growth, different methods have been developed to overcome this "time-scale problem". A widely used technique in the case of crystal growth is the kinetic Monte Carlo method (kMC).<sup>4-8</sup> In

kMC, the long-time evolution of the system is modeled by stateto-state transitions consisting of diffusive jumps. While kMC simulations reach longer time-scales than MD simulations (typically seconds),<sup>9</sup> this method is limited by the requirement that a complete catalogue of all relevant transitions and their rate constants has to be known in advance.<sup>[Metiu]</sup> Therefore, the completeness of this catalogue depends on the intuition of the scientist applying kMC. Furthermore, not all transition mechanisms are known. Hence, the reliability of the catalogue cannot be estimated. In ref. 10, an example of unexpected diffusion behavior illustrates the caution that is necessary when presuming a certain kind of reaction mechanisms.

Another technique to relax systems over a long time-scale was proposed by Barkema *et al.*<sup>11</sup> This approach, which is referred to as "activation–relaxation technique" (ART), was designed to identify local relaxation processes in amorphous silicon. In essence, this technique consists of two steps: first, beginning from a random displacement, the system is pushed upwards the energy path (the so-called "activation"). Secondly, the system is relaxed into the adjacent energy minimum on the other side of the dividing surface. In the ART algorithm, the correctness of the described evolution of the considered system is limited by the general problem whether all relevant saddle points of the energy landscape can be found.

In transition state theory (TST) based Monte Carlo (MC) methods,<sup>12,13</sup> the dynamics of a system are described as a sequence of infrequent events. The probabilities of those events are determined by the rate constants approximated by harmonic transition state theory (HTST). In order to calculate those rate constants, all saddle points, energy minima and vibrational frequencies of the atoms need to be identified. Therefore, the

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complete sampling of the energy landscape of the system is required, which is computationally very expensive. Although no assumptions on the atomistic mechanisms need to be made and the equilibrium flux of particles through a dividing surface is approximated to a good extent,<sup>14</sup> the computational cost makes this technique hardly suitable for the simulation of the whole deposition process of crystalline structures.

A very different approach was introduced by Dereli.<sup>15</sup> By applying the so-called "dynamic Monte Carlo" or "force biased Monte Carlo" scheme, process acceleration factors of up to 100 can be achieved.<sup>16</sup> In this methodology, the chosen displacement for an atom is determined by both a random number and the force that is acting on the atom.<sup>15</sup> Grein *et al.* combined the dynamic MC algorithm by Dereli with a MD code in order to simulate the epitaxial growth of Ge on Si (001).<sup>17</sup> The MD part of the simulation is used to model the arrival of new particles at the substrate ("short term behavior"), whereas the MC part models the subsequent local equilibration between deposition events. For the deposition of Ge on Si(001), Grein *et al.* conclude that the combined MD and dynamic MC approach is capable of reproducing earlier purely MD results which required a considerably greater computational effort.<sup>17</sup>

Another kind of models, termed as "accelerated dynamics methods", is developed at the Los Alamos National Laboratory.<sup>10</sup> These methods are invented to extend the time-scale of MD simulations. As for ordinary MD simulations, no prior assumptions on reaction mechanisms are needed. Therefore, the true dynamics of the investigated system can be followed. Temperature-accelerated dynamics (TAD),<sup>18</sup> is the accelerated dynamics method with the greatest boost factor.<sup>10</sup> By increasing the temperature of the system, the transitions will be observed after a shorter simulation time. The behavior of the system at high temperature  $(T_{high})$  is then extrapolated to the temperature of interest ( $T_{low}$ ). The higher the ratio of  $T_{high}$  to  $T_{low}$ , the greater the boost factor.<sup>19</sup> The extrapolation to  $T_{\text{low}}$  requires that the observed transitions obey the HTST, i.e., TAD cannot be applied to systems with strong anharmonic effects.<sup>18</sup> Since anharmonic effects become important at high temperature, the value of  $T_{\text{high}}$ is limited.<sup>18</sup> Therefore, a great boost factor cannot be obtained by TAD for systems with high  $T_{low}$ .

In this paper, we present a new method for the simulation of adatom surface processes during crystal growth. Neither do prior assumptions have to be made, nor is the system temperature limited. This fast algorithm is based on the ideas of the Metropolis Monte Carlo (MMC) algorithm which was developed in the 1950's.<sup>20</sup> In a recent publication, Taguchi *et al.* describe a combination of a MD model and the MMC algorithm for the simulation of amorphous SiO<sub>2</sub> thin film growth.<sup>21</sup> Analogous to our approach, as will be explained below, the alternating MD and MMC simulations are applied for, respectively, short-time-scale particle impacts and slow processes between two impacts.

The MMC method does not take activation barriers into account; the system is allowed to evolve based on thermodynamic properties of the system. In ref. 21 though, it is shown that the combination of a MD and the MMC model is capable of simulating the growth of films with properties consistent with experimental observations. Our MMC implementation is in general developed for the simulation of crystal growth by plasmaenhanced chemical vapor deposition (PE-CVD) when coupled to a MD model. To theoretically study crystal growth by PE-CVD, two stages of the deposition process need to be simulated: first, the simulation of growth species impacting a substrate, which can be achieved by means of MD, as described above. In the MD part of the simulation, the system is isolated, *i.e.*, the total energy, the volume and the number of particles in the system are conserved. Those "NVE simulations" of the evolution of a system generate a microcanonical ensemble. An extensive description of the applied MD model can be found elsewhere.<sup>22</sup>

Subsequently, surface relaxation processes have to be simulated, for which the presented MMC algorithm can be applied. In contrast to the deterministic MD simulations, MC simulations are driven by random numbers, and are therefore probabilistic. In MMC simulations, NVT ensembles are generated based on the sampling of the Boltzmann distribution function. This function describes the distribution of states a system can sojourn in, premising a constant number of particles, a fixed volume and a constant temperature. *I.e.*, canonical ensembles are generated.

In MMC simulations, the system evolves by random displacements ("moves") of the atoms the system consists of. Depending on the energy change the system encounters by a random displacement, this move is accepted or rejected. In essence, the Metropolis method is a Markov process in which a random walk is constructed. This random walk was commonly recognized as the correct representation of the single-particle diffusion process in a homogeneous and isotopic medium with no external forces and a suitably small step size.<sup>23</sup> Kikuchi *et al.* showed that the Metropolis Monte Carlo algorithm can be applied to the description of the detailed time-development of diffusive systems,<sup>24</sup> even for anisotropic and inhomogeneous diffusive systems.<sup>25</sup>

In the presented algorithm, the number of atoms that take part in the random walk, is restricted: the only atoms that are allowed to move are the non-crystalline adatoms and their neighbors. This restriction enables the fast simulation of adatom surface processes, such that coupling with a MD model permits the simulation of the whole deposition process of crystalline structures.

In the following, the Metropolis Monte Carlo method and its implementation are explained. To illustrate the performance of the algorithm, examples of combined molecular dynamics and Metropolis Monte Carlo (MD-MMC) simulations are shown.

The examples presented below and the used model structures throughout the discussion are hydrocarbon species at diamond substrates, since the application of the presented algorithm is part of a theoretical study of the growth mechanisms of (ultra)-nanocrystalline diamond ((U)NCD) films. (U)NCD films have recently received a lot of attention due to their unique combination of physical and chemical properties.<sup>26</sup> Until now, little is known about the growth mechanisms of these diamond structures on atomistic level. Nevertheless, the application of the method presented in this paper is not restricted to the growth of diamond structures.

## 2. Method

As explained above, the proposed MMC implementation is coupled to a MD code in order to simulate the whole deposition process of crystalline structures. The MD simulation of a particle impact, is followed by a MMC simulation. The term "combined



Fig. 1 Schematic illustration of combined molecular dynamics (MD, light gray) and Metropolis Monte Carlo (MMC, dark gray) simulations. The MD and MMC parts are applied alternately for the simulation of particle impacts and the simulation of surface relaxation processes, respectively.

MD-MMC simulation" refers to the alternation of MD and MMC simulations. In Fig. 1, the combination of the two techniques is illustrated.

A MMC move consists of two stages:<sup>20</sup> first, a randomly chosen displacement is assigned to one atom of the system (a "trial move"). This transition of the original configuration m to the trial configuration n is denoted as  $m \rightarrow n$ . The second stage is the decision whether the trial move is accepted or rejected.

According to the MMC scheme, the trial position of an atom  $(x_n, y_n, z_n)$  is determined as follows from its original position  $(x_m, y_m, z_m)^{:20}$ 

$$x_n \to x_m + \alpha^* (2^* \xi_1 - 1.0)$$
  

$$y_n \to y_m + \beta^* (2^* \xi_2 - 1.0)$$
  

$$z_n \to z_m + \gamma^* (2^* \xi_3 - 1.0)$$
(1)

In the equations,  $\alpha$ ,  $\beta$  and  $\gamma$  represent the maximum allowed displacements in *x*-, *y*- and *z*-directions, respectively.  $\xi_i$  are random numbers  $\in [0,1]$ .

The change of the potential energy  $\Delta E = E_n - E_m$  caused by the random displacement determines whether the trial configuration *n* is accepted or rejected. If the potential energy of the configuration *n* is equal to or lower than the original potential energy ( $\Delta E \leq 0$ ), the trial move is accepted.

If  $\Delta E > 0$ , a transition probability  $P_m \rightarrow n$  is calculated.  $P_m \rightarrow n$  is derived by the Boltzmann distribution function:<sup>27</sup> the occupation probability  $P_m$  for a state *m* of a canonical ensemble is given by

$$P_m = \frac{1}{Z} e^{-E_m/k_{\rm B}T} \tag{2}$$

Here,  $E_m$  represents the energy of state m, T is the temperature of the system, and  $k_B$  is Boltzmann's constant. Z is the so-called partition function,  $Z = \sum e^{-E_j/k_BT}$ .

The transition probability  $P_m \rightarrow n$  is then the ratio of  $P_n$  to  $P_m$ <sup>20</sup>

$$P_{m \to n} = \frac{\frac{1}{Z} e^{-E_n/k_{\rm B}T}}{\frac{1}{Z} e^{-E_m/k_{\rm B}T}} = e^{-\Delta E/k_{\rm B}T}, \Delta E = E_n - E_m$$
(3)

A random number  $\xi_4 \in [0,1]$  determines if the trial configuration is accepted (accept if  $\xi_4 \leq P_{m \rightarrow n}$ ).

A flow chart of the MMC implementation can be found in Fig. 2 and will be discussed below.

#### 2.1 Identification of the moving atoms

Consider a system consisting of a fixed number of atoms. In general, all atoms of the system may be involved in infrequent



**Fig. 2** Flow chart of the MMC simulation proposed in this work for the model structure (see text). The configuration that is subjected to the first MMC cycle, is the resulting configuration of a MD simulation of hydrocarbon species impacting a diamond surface. A description of those MD simulations can be found in section 3.

moves over barriers in their neighborhood. However, as stated by Kaukonen *et al.*, the number of atoms that are explicitly considered in the simulation of relaxation processes, may be restricted to a certain atom type or a sub-region of the full system in order to study only such processes, and prevent the simulation of other events that might interfere with the processes that are subject of the investigation.<sup>14</sup> Graphitization of the diamond bulk is an example of a relaxation event that would be simulated if the number of considered atoms in our MMC simulation is not restricted. Since we are not interested in the simulation of graphitization and it could interfere with adatom surface processes, bulk diamond atoms of the considered system will not be allowed to be displaced in the MMC simulation. Analogous to other Monte Carlo approaches,<sup>11-13,28</sup> the rearrangement in the local environment of the adatoms is taken into account in our model. Therefore, besides the adatoms (i.e., the atom type we are interested in), all neighbors of the adatoms (i.e., the local environment of the adatoms) are allowed to move. Hence, all adatoms need to be identified before the first MMC cycle is carried out. Atoms are classified as adatoms if they are not part of the crystalline phase. To decide whether an atom is present in the crystalline phase, the coordination and type of the atom, its neighbors and the neighbors of its neighbors are taken into account. In the case of a growing diamond structure, all carbon atoms that are part of the bulk diamond structure and all hydrogen and carbon atoms that are part of the (partially) hydrogenated diamond surface are considered to be present in the crystalline phase. For instance, a four coordinated carbon atom is considered to be part of the crystalline phase, if it is coordinated by four carbon atoms ("the neighbors") which, in their turn, are each coordinated by four carbon atoms ("the neighbors of the neighbors").

More general, relaxation processes of non-crystalline phases as grain boundaries or dislocations can be simulated; the atoms that are part of the bulk, but not present in crystalline phase, will be allowed to be displaced during the MMC simulation and join the adatoms list, though, in this case, "adatom" is not applicable in the strict sense of the term.

To take local rearrangements caused by moving adatoms into account, the list of adatoms is extended by the neighbors of the adatoms. Furthermore, also clusters of adatoms are identified in order to allow collective surface diffusion of polyatomic clusters. In this model, clusters are defined as groups of adatoms that are connected by chemical bonds. In contrast to the adatoms, the list of neighbors and clusters is updated after every accepted MMC move. The adatoms, clusters and neighbors of adatoms are allowed to be displaced and denoted as "movers".

After the update of the movers list, one of the movers is chosen randomly to carry out a trial move.

### 2.2 Random displacements

Before a trial move can be carried out for the randomly chosen mover, we need to specify the maximum allowed displacement in *x*-, *y*- and *z*-direction. In our model structure consisting of adatoms at a diamond substrate surface, the *z*-direction is defined as the vertical growth direction of the structure, and thus the substrate surface is parallel to the  $\{x,y\}$  plane. Therefore, the maximum *x*- and *y*-displacements are equal ( $\beta = \alpha$  in eqn (1)).

The optimum values for  $\alpha$  and  $\gamma$  need to obey two requirements: they have to (i) provide a good sampling of the phase space, and (ii) allow a short simulation time. Frenkel *et al.* introduced the following criterion for the optimum maximum displacement values:<sup>2</sup> the optimum maximum displacements lead to the highest sum of the squares of all accepted trial displacements per computing time. The sum of accepted trial displacements is a measure for the distance covered in the configuration space; the higher this distance, the lower the statistical error of the computed quantities.

If the maximum displacements are large, it is very probable that the resulting configuration will have a high energy and the trial move will be rejected. On the other hand, if the maximum displacements are very small, the change in potential energy is very likely to be small and most of the trial moves will be accepted, but a lot of MMC cycles will be needed to reach the final configuration. Therefore, both a too high and a too low maximum displacement will increase the calculation time.

To identify the optimum values of  $\alpha$  and  $\gamma$ , we carried out MMC simulations with varying values of  $\alpha$  and  $\gamma$ . According to our model structure, we simulated the evolution of adatoms on partially hydrogenated diamond (100)2 × 1 and (111)1 × 1 surfaces with varying values of  $\alpha$  and  $\gamma$ . Note that the (100) and (111) surfaces are the two most important surfaces for diamond.<sup>29</sup> The upper limit of  $\alpha$  was chosen according to the lattice



**Fig. 3** Partially hydrogenated diamond  $(100)2 \times 1$  (a) and diamond  $(111)1 \times 1$  (b) surfaces with a carbon adatom. Crystalline carbon atoms, dangling bonds and the carbon adatom are indicated by gray, green and red spheres, respectively. The diamond structures used for the simulations contain 814 (diamond  $(100)2 \times 1$ ) and 830 atoms (diamond  $(111)1 \times 1$ ). For clarity reasons, only the three topmost atom layers are shown. The configurations for the C<sub>2</sub> and C<sub>3</sub> adatoms are analogous to the structures shown in this figure, regarding the place and number of the dangling bonds and bonds of the adatoms to the surface.



**Fig. 4** Sum of the squares of all accepted trial displacements  $(d_{\text{accepted}^2})$  per computing time  $(t_{\text{calc}})$ , summed for C, C<sub>2</sub> and C<sub>3</sub> on (a) partially hydrogenated diamond  $(100)2 \times 1$  and (b) partially hydrogenated diamond  $(111)1 \times 1$ . The black areas indicate values below 0.17 Å<sup>2</sup> s<sup>-1</sup> (a) and 0.10 Å<sup>2</sup> s<sup>-1</sup> (b), respectively. The white areas indicate the areas with the highest values (0.34 Å<sup>2</sup> s<sup>-1</sup> and 0.27 Å<sup>2</sup> s<sup>-1</sup> for (a) and (b), respectively).

constant of the diamond unit cell (a = 3.567 Å),<sup>30</sup> *i.e.*, for  $\alpha = 3.6$  Å, each  $\{x, y\}$  point within the area of the diamond unit cell is within the reach of the MMC simulation. On the other hand, the upper limit of  $\gamma$  ( $\gamma = 1.0$  Å) covers the maximum *z*-distance between the first two carbon atom layers for diamond (0.89 Å and 0.51 Å for hydrogenated diamond (100)2 × 1 and (111)1 × 1, respectively).<sup>31</sup>

As indicated in ref. 22 and 32, different species, containing a different number of atoms, may contribute to the growth of (U)NCD. Therefore, we calculated the sum of the squares of all accepted trial displacements per computing time for C,  $C_2$  and  $C_3$ test species on partially hydrogenated diamond (100)2 × 1 and (111)1 × 1 surfaces (see Fig. 3). The initial configurations for the MMC simulations are obtained by MD simulations of impacting species on the diamond surfaces. The detailed description of those MD simulations can be found in section 3. The species form one bond with the diamond surface, which is the most probable for substrate temperatures between 800 and 1100 K.<sup>22</sup> The calculation of the sum of the squares of all accepted trial displacements per computing time is carried out 1000 times for each species on each diamond surface.

From Fig. 4, we can conclude that the optimum values of  $\alpha$  and  $\gamma$  are, respectively, 2.8 Å and 0.6 Å for a diamond (100)2 × 1 surface, and 2.8 Å and 0.8 Å for a diamond (111)1 × 1 surface.

### 2.3 Calculation of the potential energy

After the trial displacement is chosen, the energy change caused by the trial move is calculated. For the calculation of the potential energy, we apply the well-known Brenner potential for hydrocarbons.<sup>33</sup>

The Brenner potential is an empirical potential function for the description of (hydro)carbon structures. In the Brenner potential, the potential energy is written as a sum over bond energies between couples of atoms, which are determined by repulsive and attractive components. The repulsive and attractive components are function of the scalar separation between the two considered atoms. The value of the bond energy is also determined by the "bond order" function, which models the many-body chemistry and contains a correction function that accounts for the different chemistry of hydrogen and carbon. Furthermore, the repulsive and attractive components are multiplied by the value of the socalled "cutoff function". The cutoff function is introduced to limit the potential range to first neighbors only. The attractive and repulsive components are not affected by the cutoff function for interatomic distances smaller than the inner cutoff radius (*i.e.*, 1.7 and 1.3 Å for C–C and C–H interactions, respectively), since the cutoff function value equals 1 for this domain. For interatomic distances greater than the outer cutoff radius (i.e., 2.0 and 1.8 Å for C-C and C-H interactions, respectively), the interaction between the two atoms is not taken into account for the calculation of the binding energy; the cutoff function value equals 0. The cutoff function value decays smoothly from 1 to 0 between the inner and outer cutoff radii.

The cutoff function is used to define the bonding connectivity between atoms of the system. The number of bonds a given atom is involved in, is calculated as the sum of cutoff function values resulting from the scalar distances between the considered atom and the other atoms of the system.

Dyson *et al.* showed that the Brenner potential, in contrast to other empirical potential functions, describes very well the structure of diamond surfaces in agreement with quantum mechanical calculations.<sup>1</sup>

Based on the calculated energy difference, the trial configuration is accepted or rejected (see above). If the trial move  $m \rightarrow n$ is accepted, a new MMC cycle for the new configuration *n* can be carried out. If the trial move is rejected, a new MMC cycle for the original configuration *m* will be carried out.

### 2.4 Completion of the MMC simulation

During the MMC simulation, the energy of the system decreases. After a certain number of MMC cycles, the energy stagnates: no



Fig. 5 Schematic illustration of the potential energy *versus* the number of MMC cycles carried out. The configuration is in its final state, as soon as the number of adjacent rejected moves equals the number of moves from the start until the last accepted trial move (x). Typically, 10<sup>4</sup> to 10<sup>5</sup> MMC cycles are carried out until convergence is reached.

new configurations will be accepted anymore, and the energy of the system is "converged". Depending on the system, the number of cycles to reach convergence differs. Therefore, we implemented the following convergence criterion: the simulation stops, if the number of adjacent rejected moves equals the number of moves from the start until the last accepted trial move (see Fig. 5). Testing different multiples (up to four) of the last accepted trial move before the simulation stops, showed that the convergence criterion as illustrated in Fig. 5 is strict enough: for less than 1% of the MMC simulations, a higher multiple leads to a lower energy. In order to save computational cost, the lowest multiple (one) is chosen.

However, if the convergence criterion is applied from the first MMC cycle, the MMC simulation is very likely to stop after a few MMC cycles. For instance, the MMC simulation stops if the first trial move is accepted and the following two are rejected. Therefore, a minimum number of MMC cycles (*e.g.* 1000) has to be carried out before the convergence criterion is applied. Depending on the decrease of the potential energy that can be achieved by the MMC simulation,  $10^4-10^5$  MMC are needed. The more energetically unfavorable the starting configuration is, the more MMC cycles need to be carried out until convergence is reached, as will be shown below.

# **3.** Application of the algorithm: adatoms at diamond surfaces

To illustrate the performance of the MMC algorithm, we present here results of combined MD-MMC simulations that follow the evolution of adatoms at growing diamond surfaces.

Our previous MD study of the reaction behavior of various hydrocarbon species at diamond surfaces<sup>22</sup> and earlier studies of

the concentration of these species in the plasma by May *et al.*<sup>32</sup> implicate that C, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub>H<sub>2</sub> are the most important growth species for UNCD growth within their C<sub>x</sub>H<sub>y</sub> series (x = 1-4). For NCD growth, the more hydrogen rich species CH<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>2</sub>, and C<sub>4</sub>H<sub>2</sub> appear to be the most important growth species.<sup>22</sup>

To investigate the surface processes of hydrocarbon species at diamond (100)2  $\times$  1 and diamond (111)1  $\times$  1, combined MD-MMC simulations are carried out, consisting of two distinct parts. First, the impact of the hydrocarbon species on a partially hydrogenated diamond surface  $(T_{sub} = 1100 \text{ K})^{22}$  is simulated by means of MD. The partially hydrogenated diamond  $(100)2 \times 1$ and  $(111)1 \times 1$  substrates contain, respectively, 900 and 768 carbon atoms, and, in addition, 47 and 61 hydrogen atoms belonging to the hydrogenated surfaces. The number of hydrogen atoms implies the presence of three non-passivated atoms of the highest carbon layer, *i.e.*, three dangling bonds at the diamond surface. The lowest two atomic layers of the diamond substrates (100 and 128 carbon atoms for diamond (100) and (111), respectively), are kept static in order to anchor the simulation cell, preventing translation of the cell due to momentum transfer from impacting particles. The construction and temperature control of the diamond substrates is extensively discussed in ref. 22. The simulated impacts of the hydrocarbon species are normal to the diamond surface, and close to a dangling bond at the surface, *i.e.*, a reactive site that is created by hydrogen abstraction. The initial translational, rotational and vibrational energies that are laid on, correspond to a gas temperature of 2120 K above the substrate surface.<sup>32</sup> The initial distance of the impacting particle above the surface is at a distance for which the interaction energy between the surface atoms and impacting species can be neglected. Each impact is followed for 2.0 ps, using variable time-steps between  $10^{-6}$  and  $10^{-4}$  ps. Periodic boundary conditions are applied in  $\pm x$ - and  $\pm y$ direction, and no heat bath is used.

To investigate the further evolution of the stuck radical, a MMC simulation follows the MD simulation of the particle impact, according to the description in section 2. The simulations that have been carried out, illustrate one cycle of a combined MD-MMC simulation for the growth of (U)NCD. During one MD-MMC cycle, typically 1 to 10 adatoms impact the surface and further undergo adatom surface relaxation processes. This situation corresponds to experimental conditions during PE-CVD of (U)NCD: the flux of hydrocarbon species to the surface can be estimated to be  $10^{15}$  cm<sup>-2</sup>s<sup>-1</sup>.<sup>34</sup> This implies that for a simulation cell with a surface of 20 by 20 Å, the time between two impacts is in the order of  $10^{-2}$  s. Therefore, the simulation of relaxation events after a simulated time of 2.0 ps by means of MD, applies only to a few adatoms.

To verify the resulting structures from the MMC simulations and to demonstrate the power of the implemented MMC algorithm, additional MD simulations are carried out: in this paper, besides the MMC simulations, the evolution of the stuck hydrocarbon species at the diamond surface (*i.e.*, the input configuration of the MMC simulation) is followed by means of MD as well. For these MD simulations, the same simulation conditions are applied as for the simulation of the impacts regarding the variable time step, periodic boundary conditions and temperature control. In the case of the UNCD growth species, the MD simulations lead to the same configurations as the MMC simulations within a reasonable simulation time, as will be shown and discussed below. The MMC simulations of the NCD growth species at the diamond surface predict bond breaking between carbon and hydrogen adatoms such that reactive sites are created. During PE-CVD of the diamond, this bond breaking is realized for example by hydrogen abstraction ("etching") by impacting hydrogen atoms from the plasma.<sup>35</sup> Therefore, the predicted bond breaking in our MMC simulation is not an unrealistic mechanism. In MD simulations though, the spontaneous hydrogen-carbon bond breaking cannot be simulated within a reasonable calculation time (less than two months). To enable the pure comparison of the structures obtained by MMC simulations and MD simulations, and thus without simulating hydrogen abstraction by other impacting species, we focus in this paper on the relaxation behavior of UNCD growth species.

To observe growth of diamond crystal structures, sufficient carbon adatoms need to be present to enable the formation of new carbon six-rings that are characteristic of the diamond structure. For the flat diamond surfaces, at least one (diamond (100)2 × 1) and three (diamond (111)1 × 1) carbon adatoms are required. In this study, three exemplary adatom arrangements, covering the species that are the most important for UNCD growth (see above), are investigated: the adatom surface relaxation behavior of C and C<sub>2</sub>H<sub>2</sub> at diamond (111)1 × 1, C and C<sub>4</sub>H<sub>2</sub> at diamond (111)1 × 1 and C<sub>3</sub> at diamond (100)2 × 1 are discussed below. As expounded in section 2.2, the MMC simulation parameters  $\alpha$  and  $\gamma$  are chosen to be 2.8 and 0.6 Å (diamond (100)2 × 1) or 2.8 and 0.8 Å (diamond (111)1 × 1), respectively.

### 3.1 A C atom and a $C_2H_2$ molecule at diamond (111)1 $\times$ 1

The configuration as shown in Fig. 6a is obtained by a MD simulation of consecutive impacts of a C atom and a C<sub>2</sub>H<sub>2</sub> molecule on a partially hydrogenated diamond (111)1  $\times$  1 surface. Before the impacts, this diamond surface contains three dangling bonds that are located close to each other; *i.e.*, Fig. 3b represents the configuration after the impact of the carbon atom and before the impact of the C<sub>2</sub>H<sub>2</sub> molecule. As shown in Fig. 6a, both the C atom and the C<sub>2</sub>H<sub>2</sub> molecule are bonded by one bond to the diamond  $(111)1 \times 1$  surface, which is the most probable configuration at substrate temperatures relevant for the deposition of UNCD ( $T_{sub} > 700 \text{ K}$ ).<sup>22</sup> The simulation cell contains five adatoms: three carbon adatoms, in Fig. 6 highlighted in red, and two hydrogen atoms that are bonded to carbon adatoms. At the start of the MMC simulation, there are three additional movers: the two diamond surface atoms that are bonded to the adatoms ("the neighbors") and one cluster (originating from the  $C_2H_2$ molecule). The carbon atom is not classified as a cluster since it does not have neighbors that are adatoms, too (see section 2.1).

In Fig. 7, the progress of the potential energy and calculation time are shown. During the MMC simulation, the potential energy decreases by 6.24 eV from -5532.62 to -5538.86 eV (see Fig. 7). To reach convergence, 391046 MMC cycles, of which 47 accepted trial moves, were carried out during 356 min. The labels a–e in Fig. 7 correspond to the configurations shown in Fig. 6a–e.



**Fig. 6** Selected snapshots illustrating the evolution of a C atom and a  $C_2H_2$  molecule on a partially hydrogenated diamond (111)1 × 1 surface under the influence of the MMC algorithm. The white, gray and red spheres indicate hydrogen atoms, crystalline carbon atoms and carbon adatoms, respectively. (a) Side view of the resulting structure of adjacent MD simulations of the impact of a C atom and the impact of a  $C_2H_2$  molecule on a partially hydrogenated diamond (111)1 × 1 surface and its three topmost atom layers. (b)–(d) The three topmost layers of the structure after 484, 1564 and 3675 MMC cycles, respectively. (e) Side view of the final MMC structure and its three topmost atom layers; here, the red spheres indicate the new carbon sixring that is formed during the MMC simulation.



**Fig. 7** Potential energy ( $E_{\text{pot}}$ , solid line, left *y*-axis) and calculation time ( $t_{\text{calc}}$ , dashed line, right *y*-axis) *vs*. number of MMC cycles taken in the MMC simulation of a C atom and C<sub>2</sub>H<sub>2</sub> molecule on partially hydrogenated diamond (111)1 × 1. The labels a–e indicate the points at the potential energy curve that correspond to the snapshots in Fig. 6. The dots on the dashed line indicate accepted moves.

Fig. 6b–d illustrate the MMC simulation by selected snapshots of accepted configurations. The formation of a new carbon sixring which is characteristic of the diamond crystal structure, is shown in Fig. 6b and c. First, as can be seen in Fig. 6b, an energetically unfavorable carbon three-ring is formed. The carbon–carbon bond breaking (Fig. 6c) therefore leads to a decrease of the potential energy by 1.90 eV (see Fig. 7). After this MMC trial move, no further carbon–carbon bonds are broken or formed. Nevertheless, Fig. 6d shows that one of the hydrogen adatoms is displaced, such that the two hydrogen adatoms are bonded to the same carbon adatom. Fig. 6e shows the final MMC configuration. The formation of the diamond sixring pursues the diamond crystal structure, that is, the three carbon adatoms are repositioned according to the diamond structure. Therefore, it can be concluded that growth of the diamond substrate is simulated.

As explained above, additional MD simulations have been carried out to verify the resulting configurations from the MMC simulations. The starting configuration of the MD simulation (shown in Fig. 8a) is identical to the starting configuration of the MMC simulation (see Fig. 6a). In Fig. 8, the evolution of the stuck C atom and  $C_2H_2$  molecule at the diamond (111)1  $\times$  1 surface under the influence of a MD simulation is shown. Within a simulated time of 0.47 ps, the formation of a new diamond sixring is observed, *i.e.*, the same carbon-carbon bonds are formed as in the MMC simulation (see Fig. 8c). This diamond six-ring is formed within a MD simulation time of 47 min, whereas the MMC simulation took 1564 cycles within less than 3 min to reach the diamond six-ring (see Fig. 6c and Fig. 7). After a MD calculation time of two months (corresponding to a simulated time of  $\sim 1$  ns), no hydrogen–carbon bond is rearranged as predicted by the MMC simulation.

Whereas the MD and MMC simulations lead to the same formation of carbon–carbon bonds, the MD simulation does not reach the time-scale for which hydrogen–carbon bond breaking would be observed. Therefore, the final configuration of the MD and MMC simulations differ regarding the hydrogen–carbon bonds.

The boost factor of the MMC simulation can be estimated by the MD and MMC simulation times needed to reach the comparable configurations which are shown in Fig. 6c and 8c. The ratio of the total MD simulation time (47 min) to the MMC simulation time until the hydrogen–carbon bond is displaced (4 min) indicates a boost of about one order of magnitude. Since the hydrogen–carbon bond breaking takes more than two months MD simulation time and less than six hours MMC simulation time, the overall boost factor would be even higher.



**Fig. 8** Selected snapshots illustrating the evolution of a C atom and  $C_2H_2$  molecule on a partially hydrogenated diamond (111)1 × 1 surface under the influence of MD simulation. The white, gray and red spheres indicate hydrogen atoms, crystalline carbon atoms and carbon adatoms, respectively. Side view of the resulting structure of adjacent MD simulations of the impact of a C atom and the impact of a  $C_2H_2$  molecule on a partially hydrogenated diamond (111)1 × 1 surface and its three topmost atom layers (a) at the start of the simulation and (b) after 0.16 ps. (c) Side view of the structure and its three topmost atom layers after 0.47 ps; here, the red spheres indicate the new carbon six-ring that is formed during the MD simulation.

### 3.2 A C atom and a C<sub>4</sub>H<sub>2</sub> radical at diamond (111)1 $\times$ 1

To obtain the starting configuration for the MMC simulation of a C atom and a  $C_4H_2$  radical at diamond (111)1 × 1, two consecutive impacts were simulated by means of MD, analogous to the simulations of the impacts of a C atom and a  $C_2H_2$ molecule, as described in section 3.1. In the resulting configuration from the MD simulation (see Fig. 9a), both the C atom and the  $C_4H_2$  radical are bonded by one bond to the surface, which is the most probable configuration for the substrate temperatures that is typical of UNCD growth.<sup>22</sup> Close to the stuck C atom and  $C_4H_2$  radical, there is one dangling bond present at the diamond surface, again analogous to the configuration as described in section 3.1.

There are ten movers present at the beginning of the MMC simulation; *i.e.*, each of the adatoms, which are five carbon adatoms and two hydrogen adatoms originating from the impacting radicals, as well as one cluster ( $C_4H_2$ ) and two

diamond surface atoms, *i.e.*, one bonded to the lonely carbon adatom and the other bonded to the  $C_4H_2$  cluster.

In Fig. 10, the potential energy as a function of the MMC cycles carried out, is shown. The potential energy decreases by 2.74 eV from -5550.33 to -5553.07 eV within a simulation time of 20 min. 21688 MMC trial moves are carried out, including 17 accepted moves. The decrease of the potential energy that can be achieved during the MMC simulation (2.74 eV) is lower than in the case of C and C<sub>2</sub>H<sub>2</sub> at diamond (111)1 × 1 (6.24 eV, see section 3.1); hence, fewer MMC cycles are needed to reach convergence.

In Fig. 9b–d, selected snapshots of the MMC simulation show how a new diamond six-ring is formed during the MMC simulation. First (see Fig. 9b), one of the carbon adatoms originating from the  $C_4H_2$  cluster is displaced such that one carbon–carbon bond in the  $C_4H_2$  cluster is broken, and one new carbon–carbon bond is formed between the moving carbon adatom and the formerly lonely carbon adatom. As can be seen in Fig. 9b, three



**Fig. 9** Selected snapshots illustrating the evolution of a C atom and a  $C_4H_2$  radical on a partially hydrogenated diamond (111)1 × 1 surface under the influence of the MMC algorithm. The white and gray spheres indicate hydrogen atoms and crystalline carbon atoms, respectively. The red and blue spheres represent carbon adatoms; in blue spheres highlight the carbon adatoms that were displaced during the MMC cycle after which a snapshot was taken. (a) Side view of the resulting structure of adjacent MD simulations of the impact of a C atom and the impact of a  $C_4H_2$  radical on a partially hydrogenated diamond (111)1 × 1 surface and its three topmost atom layers. (b)–(d) The three topmost layers of the structure after 452, 1192 and 1196 MMC cycles, respectively. (e) Side view of the final MMC structure and its three topmost atom layers; here, the red spheres indicate the new carbon sixring that is formed during the MMC simulation.

of the carbon adatoms and three carbon atoms originating from the diamond substrate form a carbon six-ring after 452 MMC cycles: the diamond structure is pursued. After this accepted trial move, the  $C_4H_2$  cluster does not exist anymore. Instead, there are two new clusters: a  $C_2H$  cluster that was formed by the carbon– carbon bond breaking within the  $C_4H_2$  cluster, and is not bonded to the diamond surface at this stage of the MMC simulation, and a  $C_3H$  cluster that originates from the new carbon–carbon bond. From Fig. 10, where the labels a–e point to the value of the potential energy that correspond to the configurations shown in Fig. 9a–e, it can be seen that the trial move leads to a decrease of the potential energy of 0.14 eV. After 1196 MMC cycles (see Fig. 9d), the  $C_2H$  cluster moves towards the carbon six-ring, such that the carbon–carbon bond which was broken after 452 trial moves (Fig. 9b) is resumed. The greatest fraction of the MMC



**Fig. 10** Potential energy ( $E_{pot}$ , solid line, left *y*-axis) and calculation time ( $t_{calc}$ , dashed line, right *y*-axis) *vs*. number of MMC cycles taken in the MMC simulation of a C atom and C<sub>4</sub>H<sub>2</sub> radical on partially hydrogenated diamond (111)1 × 1. The labels a–e indicate the points at the potential energy curve that correspond to the snapshots in Fig. 9). The dots on the dashed line indicate accepted moves.

cycles is further spent on the rearrangement of adatom positions without any new bond breaking or forming (see Fig. 9d–e). This rearrangement of the atomic positions between MMC cycles 1196 and 10843 causes a decrease of the potential energy of 1.92 eV (see labels (d) and (e) in Fig. 10).

In Fig. 11, the evolution of the C atom and C<sub>4</sub>H<sub>2</sub> radical as predicted by the MD simulations is shown. To compare the resulting configurations of the MD and MMC simulations, the input configuration of the MD simulation (Fig. 11a) is identical to the one used for the MMC simulation (Fig. 9a). As can be seen from Fig. 11c, the resulting configurations of the MD simulation exhibits the same carbon-carbon and hydrogen-carbon bonds. However, whereas the final configurations of the MD and MMC simulations are very similar, the formation of the new diamond six-ring is different. In the MMC simulation, the carbon-carbon bonds were broken and resumed. In contrast to that, no bonds are broken during the MD simulation. This indicates that the correct description of the time-development of diffusive systems by MMC algorithms<sup>24</sup> is indeed true for the products of a reaction path, but not for transitional configurations. As mentioned in section 1, activation barriers are not taken into account, which explains the differences of the transitional configurations as put forward by the MMC and MD simulations.

The MMC simulation time (20 min) is considerably shorter than the MD simulation time: it took 169 min to simulate 1.64 ps by means of MD, indicating a boost of almost one order of magnitude.

### 3.3 A C<sub>3</sub> radical at diamond (100)2 $\times$ 1

In Fig. 12a, the resulting configuration from the MD simulation of an impacting  $C_3$  radical is shown. The  $C_3$  radical is bonded by one bond to the diamond surface, which is the most probable configuration during the growth of UNCD.<sup>22</sup> Close to the  $C_3$ radical, two dangling bonds are present at the diamond surface (see Fig. 3a). At the beginning of the MMC simulation, there are five movers that are allowed to undergo a trial move in the first MMC cycle: each of the three adatoms originating from the  $C_3$ radical, the adatom cluster consisting of the three adatoms, and



**Fig. 11** Selected snapshots illustrating the evolution of a C atom and  $C_4H_2$  radical on a partially hydrogenated diamond (111)1 × 1 surface under the influence of a MD simulation. The white, gray and red spheres indicate hydrogen atoms, crystalline carbon atoms and carbon adatoms, respectively. Side view of the resulting structure of adjacent MD simulations of the impact of a C atom and the impact of a  $C_4H_2$  molecule on a partially hydrogenated diamond (111)1 × 1 surface and its three topmost atom layers (a) at the start of the simulation and (b) after 1.08 ps. (c) Side view of the structure and its three topmost atom layers after 1.68 ps; here, the red spheres indicate the new carbon six-ring that is formed during the MD simulation.



**Fig. 12** Selected snapshots illustrating the evolution of a  $C_3$  radical on a partially hydrogenated diamond  $(100)2 \times 1$  surface under the influence of the MMC algorithm. The white, gray and red spheres indicate hydrogen atoms, crystalline carbon atoms and carbon adatoms, respectively. (a) Side view of the resulting structure of a MD simulation of an impacting  $C_3$  radical on the partially hydrogenated diamond  $(100)2 \times 1$  surface and its three topmost atom layers. (b)–(d) The three topmost layers of the structure after 514, 2280 and 11979 MMC cycles, respectively. (e) Side view of the final MMC structure and its four topmost atom layers; here, the red spheres indicate the new carbon six-rings formed during the MMC simulation.

the only neighbor of the adatoms, that is the diamond surface carbon atom to which the adatom cluster is bonded.

As can be seen from Fig. 13, the MMC simulation causes the potential energy to decrease by 6.40 eV from -5420.52 to -5426.92 eV. To reach the final structure, 301893 MMC cycles were carried out within 252 min, including 27 accepted moves. The decrease of the potential energy is comparable to the case of C and C<sub>2</sub>H<sub>2</sub> at diamond (111)1 × 1 (6.24 eV). Therefore, the number of MMC cycles needed to reach convergence is of the same order of magnitude (10<sup>5</sup>).

Fig. 12b–d show selected snapshots to illustrate the evolution of the structure shown in Fig. 12a under the influence of the MMC algorithm. From Fig. 12b, it can be seen that during the



**Fig. 13** Potential energy ( $E_{pot}$ , solid line, left *y*-axis) and calculation time ( $t_{cale}$ , dashed line, right *y*-axis) *vs*. the number of MMC cycles taken in the MMC simulation of a C<sub>3</sub> radical on partially hydrogenated diamond (100)2 × 1. The labels a–e indicate the points at the potential energy curve that correspond to the snapshots in Fig. 12. The dots on the dashed line indicate accepted moves.

MMC simulation, one of the adatoms gains a higher coordination number: a formerly one-coordinated carbon adatoms becomes two-coordinated. This new bond between the C3 radical and the diamond surface induces the formation of a new diamond six-ring, which consists of the three carbon adatoms and three carbon atoms from the first and second atom layers of the diamond substrate. Fig. 12c shows that another adatom gains coordination; the formerly two-coordinated carbon adatom becomes three-coordinated. As can be seen in Fig. 12c, the threecoordinated carbon adatom is part of a carbon three-ring, which is an energetically unfavorable configuration. The bond breaking of the other two involved carbon atoms at the diamond surface after 11979 MMC cycles (see Fig. 12d) therefore lowers the potential energy, as can be seen from Fig. 13, where the labels a-e indicate the points at the potential energy curve that correspond to the snapshots in Fig. 12a-e. This bond breaking inserts the carbon adatom into the carbon-carbon bond at the diamond surface, which disturbs the reconstruction geometry and leads to the formation of a new diamond six-ring, i.e., the diamond crystal grows. This carbon six-ring consists of one carbon adatom and five carbon atoms originating from the first three atom layers of the diamond substrate. After accepting this MMC configuration, no new bonds are formed or broken during the MMC simulation. It can be concluded that in the resulting structure of the MMC simulation (see Fig. 12e), two new carbon six-rings are formed, which pursue the diamond crystal.

In Fig. 14, the longer-time-scale evolution of a stuck C<sub>3</sub> radical on a partially hydrogenated diamond (100)2  $\times$  1 surface by means of a MD simulation is shown which serves as starting configuration. The structure shown in Fig. 14a is identical to the structure shown in Fig. 12a, *i.e.*, the resulting structure of the simulated impact of a C<sub>3</sub> radical onto the partially hydrogenated diamond (100)2  $\times$  1 surface. As can be seen from Fig. 14, the MD simulation leads to exactly the same formation and breaking of carbon–carbon bonds as was observed in the MMC simulation. After a simulated time of 27.06 ps (Fig. 14d), no new bond formation or breaking is observed. The final structure from the MD simulation is identical to the final MMC structure. In



Fig. 14 Selected snapshots illustrating the evolution of a  $C_3$  radical on a partially hydrogenated diamond  $(100)2 \times 1$  surface under the influence of a MD simulation. The white, gray and red spheres indicate hydrogen atoms, crystalline carbon atoms and carbon adatoms, respectively. Side view of the resulting structure from a MD simulation of an impacting  $C_3$  radical on the partially hydrogenated diamond  $(100)2 \times 1$  surface and its three topmost atom layers (a) at the start of the simulation, (b) after 0.77 ps and (c) after 26.99 ps. (d) Side view of the structure and its four topmost atom layers after 27.05 ps; here, the red spheres indicate the new carbon six-rings that are formed during the MD simulation.

contrast to the short calculation time of the MMC simulation (4 h 12 min), the MD simulation took 46.5 h, indicating again a boost factor of the MMC simulation of about one order of magnitude.

### 4. Conclusions

In this paper, we present a new implementation for the simulation of adatom surface processes during crystal growth that is based on the Metropolis MC algorithm. The implementation includes a criterion for the selection of atoms that are allowed to be displaced during the simulation, and a criterion of after how many MMC cycles the simulation is stopped. When coupling the MMC model to an MD model, crystal growth by plasma-enhanced chemical vapor deposition can be simulated on the atomic scale.

We performed combined MD-MMC simulations for hydrocarbon species that are important for the growth of UNCD at partially hydrogenated diamond surfaces. After a MD simulation of the particle impacts on the diamond surfaces, the adatom surface behavior of C and  $C_2H_2$  at diamond (111)1 × 1, C and  $C_4H_2$  at diamond (111)1 × 1 and  $C_3$  at diamond (100)2 × 1 has been investigated, exemplary for adatom arrangements during the growth of UNCD. For all species, the formation of diamond sixrings is observed during the MMC simulation; pursuing thereby the diamond crystal structure. To verify these results, additional longer time-scale MD simulations have been carried out. The resulting structures are very similar to those obtained by the MMC simulations, but the MMC simulation time is typically one order of magnitude shorter than the MD simulation time, or, in other words, a boost factor of one order of magnitude is achieved.

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