

Molecular-dynamics study of the collision between a gas-phase C atom and an H atom chemisorbed on diamond surfaces

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Using first-principles molecular-dynamics simulations, we study the collision between a gas-phase C atom and an H atom chemisorbed on the diamond surfaces in a first step to understand the H-mediated diamond-film growth. We find that the chemisorption-energy-converted kinetic energy of the incoming C atom can be effectively transferred to the H atom, so that the new C atom can quickly settle on the surface. The H atom is found to shift its bonding to the new C atom, so that its original chemisorption site can be freed for the deposition of the new C atom.

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The diamond C(100) and C(111) surfaces are two of the surfaces commonly chosen for the chemical vapor deposition (CVD) growth of the technologically important diamond films. Atomic H is known to play an important role in the mediation of the growth of diamond films.¹⁻⁶ Its presence prevents C atoms from forming sp^2 graphitelike bonding arrangement. It should also act like a catalyst, i.e., it should not be bonded to the chemisorption site for an extended time during the growth process so as to block the sticking of a new C atom to the site. In other words, the atomic H mediates the settlement of the incoming C atom, but after the new C atom settles on the surface, the atomic H should remain active and be freed from its original chemisorption site not buried underneath the new carbon layer. Why the H atom has this unique property is still not known. In a previous study, Tsai, Jiang, and Lin found that H and Li atoms could destabilize a sp^2 -bonded surface structure via s -orbital coupling. On the other hand, O and F atoms with a p character do not have this property.⁷ This finding might partially explain the unique property of atomic H of preventing the surface from forming a sp^2 -bonded structure. To answer the question why the chemisorbed H atom does not block the active site on the surface for the new C atom to be bonded to the surface requires a dynamics study of how a gas-phase C atom collides and replaces the chemisorbed H atom. Since the diatomic bond strengths for C-H and C-C bonds are 3.5 and 6.3 eV, respectively,⁸ and the C-C bond is a multiple bond, the C-H bond strength may be stronger than the C-C single-bond strength. Thus, the ability for a C atom to replace a chemisorbed H atom on the diamond surface may not be understood simply by static energetics such as the potential energy surface or potential-energy barrier calculations.⁹

A direct insertion reaction in the C-H bond is well known in chemical literature and was proposed to play possibly a role in diamond growth.¹⁰⁻¹² The principal processes occurring during the CVD growth of diamond using hydrogen and the dilute concentration of hydrocarbon species were discussed by Butler and Woodin.¹³ One of the principal processes is the dissociation of the methane molecule, CH_4 , step by step to result in a dissociated C atom that reacts with the surface. In the typical plasma phase, the CH_n radicals are orders of magnitude more abundant than atomic C species.

In higher-energy plasma such as dc jets, the abundance of radicals with less H and atomic C can be increased. The numerical simulations of Zhang, Dunn-Rankin, and Taborek¹⁴ of both a hot-filament reactor and a plasma torch reactor showed that the concentration of atomic C at the substrate surface could be much higher than the concentration of CH_3 . Yu and Girshick,¹⁵ using numerical computations, showed that for very thin boundary layers (high velocities) the diamond growth is dominated by the atomic C species. The previous quantum-chemistry studies have contributed significantly to the understanding of the diamond growth. Here, we try to understand the diamond growth, in particular the exchange mechanism between the gas-phase C atom and the chemisorbed H on the diamond surface, from an atomistic point of view by molecular-dynamics (MD) simulations. The MD simulations may gain insight into how a new C atom is directly inserted in the surface C-H bond and substantiate the knowledge of the catalytic role of H in diamond growth. As a first step to understand the fundamental mechanism of the insertion of a new C atom in the surface C-H bond, we avoid the complexity of the plasma phase by considering only the atomic C species and placing its starting position in the reaction range of the surface (~ 3 Å above the surface) outside the plasma phase. We consider an initial condition of the gas-phase C atom in which this gas-phase C atom can directly collide with a chemisorbed H atom. In a future study the initial condition of the gas-phase C atom will be varied statistically or systematically.

We use a real-space density-functional MD method to simulate the approaching of a gas-phase C atom to the diamond (100) and (111) surfaces, its collision with the chemisorbed H atom, and its settlement on the surface. This MD method¹⁶⁻¹⁸ is based on the real-space norm-conserving pseudopotential method¹⁹ implemented with the Ceperley-Alder exchange-correlation potential.²⁰ The basis set is a minimal basis set similar to that used in the linear muffin-tin orbital (LMTO) method.²¹ The modified Hellmann-Feynman theorem²² is used to calculate the forces acting on every atom. The Newtonian equations of motion are solved numerically using the fifth order Gear algorithm.²³ This method has been shown to work well for semiconductors²⁴⁻²⁷ and diamond.^{7,28} The incoming C atom acquires kinetic energy when it is attracted toward the surface by the chemisorption

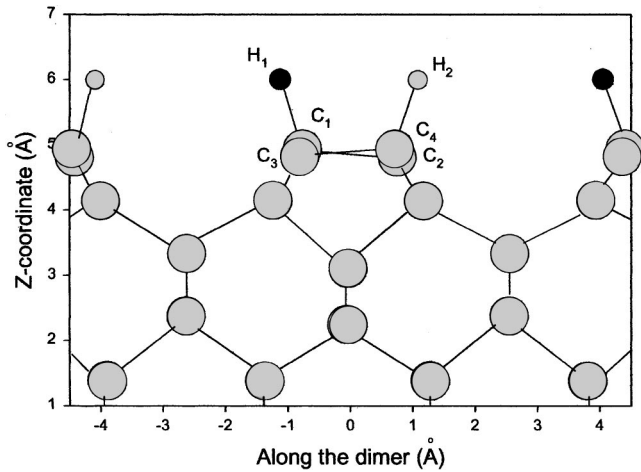
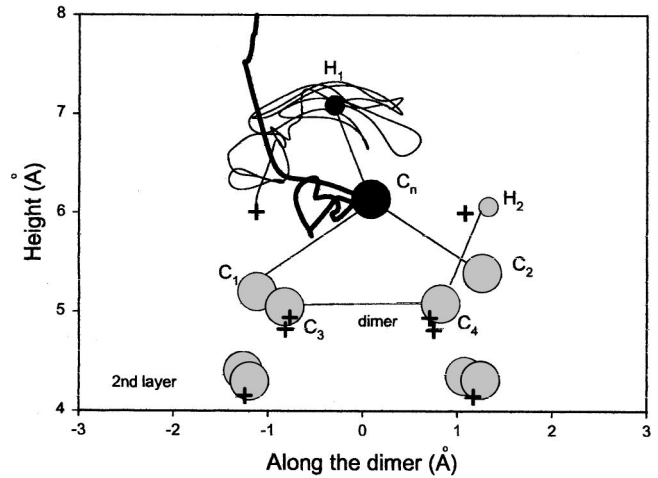


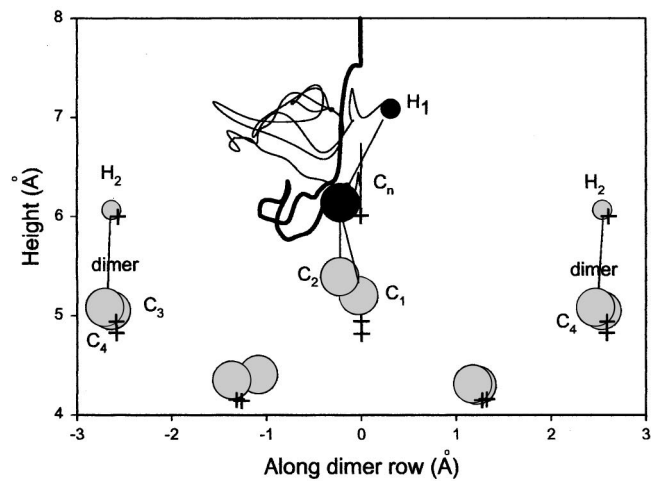
FIG. 1. Side view of the dimerized C(100) surface with $\frac{1}{2}$ ML of H adatoms. Each dimer is bonded with only one H atom. The H atoms are bonded at the left and right ends alternatively along the dimer row.

potential energy. Before the incoming C atom settles on the surface, a substantial part of its kinetic energy can be transferred to the chemisorbed atoms and atoms in the layers near the surface as heat, which then dissipates into the bulk. To simulate the heat dissipation process, we take away a part of the kinetic energy, ΔE , of the atoms in the three bottom layers at each time step according to $\Delta E = k(T - T_0)\Delta t A / \Delta Z$. Here, k is the thermal conductivity of diamond, 9900 mW/cm K.⁸ T and T_0 are the temperatures of the atoms in the bottom layers and a reference temperature, respectively. The reference temperature is assumed to be the temperature in the interior of the film and is set to be zero for simplicity. Δt is the time interval between two successive time steps. A is the area per (1×1) cell and ΔZ is the separation between a given layer and a reference layer, which is chosen as the layer beneath the bottom layer. We have chosen a six-layer supercell model with a vacuum region of about 5 Å. The theoretical lattice constant of 3.66 Å obtained in a previous study²⁷ is used. The bottom-layer atoms are attached with H atoms to saturate their dangling bonds. They are also assigned an arbitrarily large mass, so that they are bulklike. We sample only the Γ point in all simulations.

For the C(100) surface, we have chosen the (2×2) unit cell and a $\frac{1}{2}$ monolayer (ML) coverage of H atoms. The side view of the optimized surface geometry is given in Fig. 1. There are two H atoms and two C dimers per unit cell. One of the two atoms in each dimer is bonded with an H atom. The H atoms are bonded to the left and right atoms of the dimers alternatively along the dimer row as shown in Fig. 1. The dimer bond length obtained is 1.52 Å, which is very close to that of the C-C single bond, 1.54 Å.⁸ The calculated C-H bond length is 1.12 Å, which is also very close to the observed C-H bond length or sum of the C and H covalent radii of 1.09 Å.^{8,29} These results suggest that our calculations are reliable. The H-covered C(111) surface structure is chosen to be Pandey's (2×1) π -bonded chain structure chemisorbed with a $\frac{1}{4}$ ML of H atoms obtained in a previous study.⁷ We have also chosen the (2×2) unit cell for the



(a)



(b)

FIG. 2. Trajectories of C_n (thick line) and the H atom collided by C_n , H_1 (thin line) on C(100). Circles represent atomic arrangement after 296 fs of simulation. Crosses are initial atomic positions. (a) and (b) are side views into and facing the dimer row, respectively.

(111) surface. The (2×2) unit cell corresponds to a very high flux density of the incoming C atoms. The periodic boundary condition inherent in the method used prevents kinetic-energy transfer along the surface. Since this limitation underestimates the dissipation of the kinetic energy for the new carbon atom to settle, its effect is to overestimate the settlement time. Nevertheless, this effect will not affect the unique property of the atomic H to be shown in this paper. In this study, we consider not only the H atom but also the D atom in order to understand whether the mass of the chemisorbed species influences the settlement of the new C atom and the change in the local surface structure. The gas-phase C atom is simulated by placing a C atom (per unit cell) about 2 Å atop the chemisorbed H atom and is assigned an initial velocity corresponding to a temperature of 700 °C in a typical CVD growth condition. This temperature corresponds to a thermal energy of 0.08 eV, which is much smaller than the chemisorption energy of an order of 1 eV. Thus, the initial

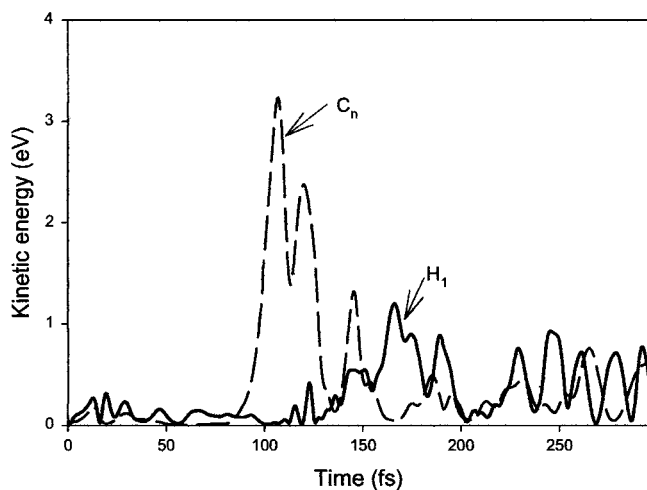


FIG. 3. The kinetic energies of C_n and H_1 as functions of time for the (100) surface.

magnitude and direction of the velocity assigned to the incoming C atom may not have significant effect on the simulation.

The trajectories of the incoming C atom, hereon denoted as C_n , and the H atom collided by C_n , denoted as H_1 , and the positions of neighboring atoms on C(100) after 296 fs of simulation are shown in Figs. 2(a) and 2(b). In these figures, atoms C_1 and C_2 are the two atoms of the dimer that is originally bonded with H_1 (as shown in Fig. 1). C_1 and C_2 can be clearly seen to separate. The H atom H_2 , which is not collided by C_n , is still bonded to the dimer formed by atoms C_3 and C_4 . C_n becomes bonded with C_1 and C_2 at the bridge site, which is the atomic site in the next layer to be grown. The kinetic energies of C_n and H_1 as functions of time are shown in Fig. 3. This figure shows that the kinetic energy of C_n increases up to about 3.3 eV, which is related to the chemisorption energy of C_n . The kinetic energy of C_n then drops down to a residual oscillation, which is expected to die

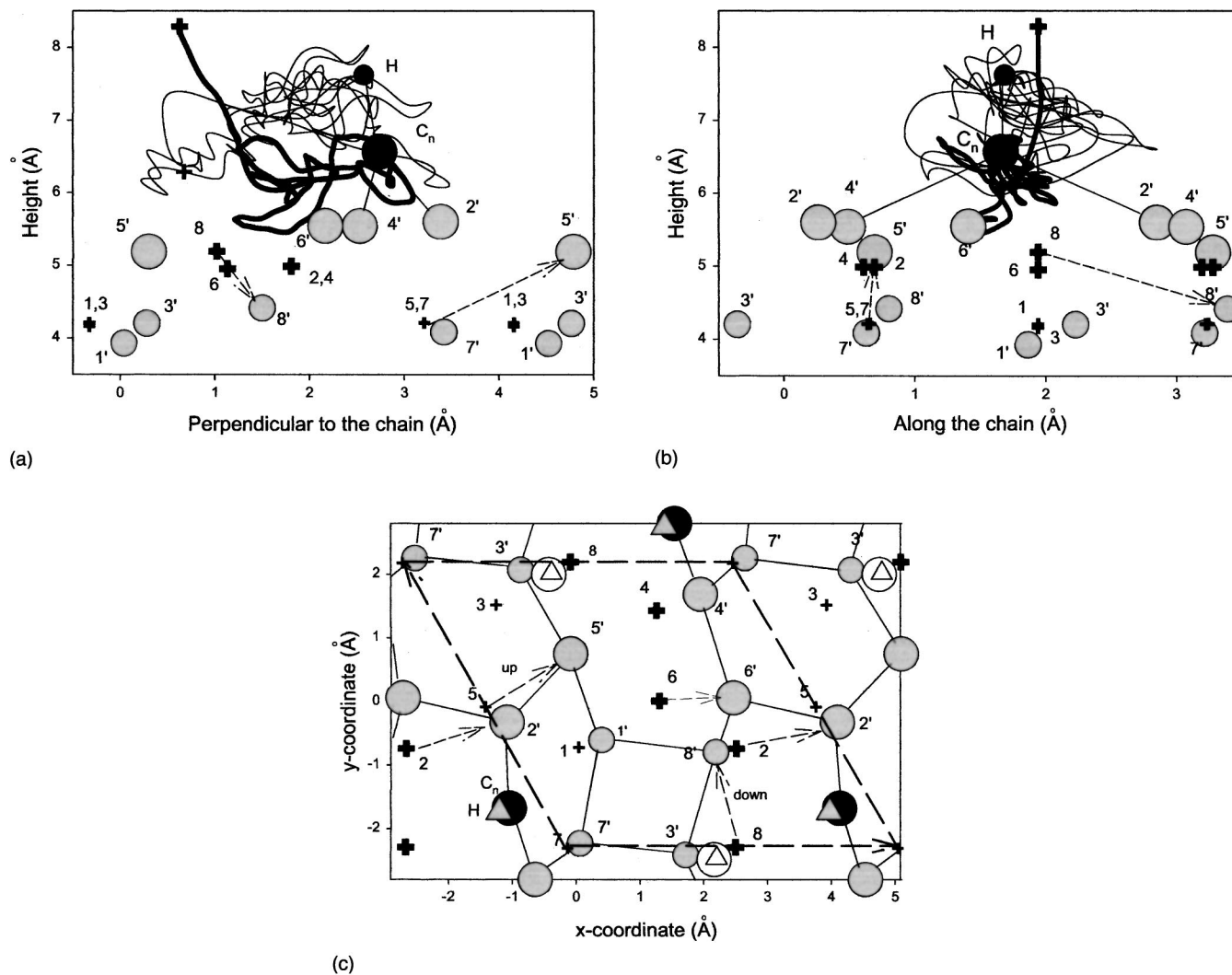


FIG. 4. Trajectories of C_n (thick line) and the H atom (thin line) on C(111). Circles represent atomic arrangement after 593 fs of simulation. Crosses are initial atomic positions. (a) and (b) are side views into and facing the π -bonded chain, respectively. (c) is the top view. In these figures, large and small circles represent first- and second-layer atoms, respectively. In (c), dashed arrows mark the displacements of atoms 2, 5, 6, and 8. The open circle and triangle mark the initial positions of C_n and the H atom, respectively. Thick dashed lines show the (2×2) unit cell.

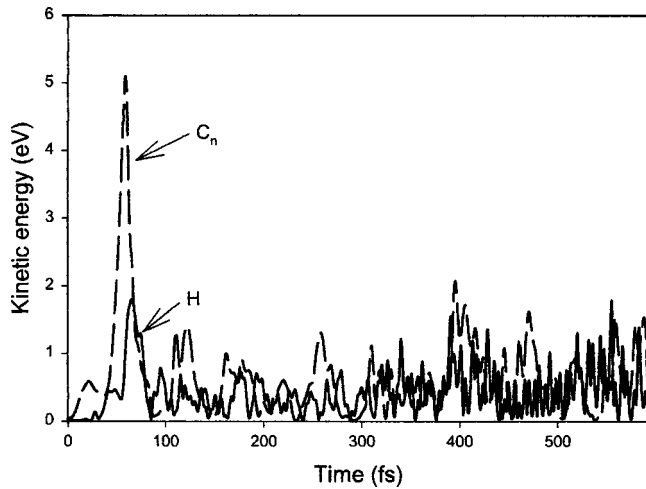


FIG. 5. The kinetic energies of C_n and H as functions of time for the (111) surface.

out gradually. On the other hand, the kinetic energy of H_1 increases up to about 1.2 eV and then oscillates and diminishes gradually. The oscillating behavior of these kinetic energies is associated with the motion of H_1 back and forth on the vacuum side of C_n . The changes of these kinetic energies also suggest that a substantial part of the chemisorption-energy-converted kinetic energy of C_n has been transferred to C surface and interior atoms. At 296 fs, C_n and H_1 still have speeds of 0.0326 and 0.0941 Å/fs, respectively, which correspond to temperatures of 5.15×10^3 and 3.60×10^3 K or 0.444 and 0.311 eV, respectively. These temperatures are still very high. However, Figs. 2(a) and 2(b) show that C_n moves around in the vicinity of the bridge site and H_1 moves around C_n on the vacuum side. Thus, we may say that C_n has settled on the bridge site. H_1 is clearly seen to move farther away from the surface and is no longer bonded to C_1 in the original dimer, but is now bonded to C_n instead. The high temperature of H_1 indicates a transfer of substantial kinetic energy from C_n to H_1 . The sum of the kinetic energies of C_n and H_1 at 296 fs, 0.755 eV, is smaller than a typical chemisorption energy of an order of 1 eV, which indicates a transfer of kinetic energy from C_n to the substrate. Our MD simulation clearly shows the replacement of the chemisorbed H atom by the gas-phase C atom. The result also shows the restoration of the original dimer to become bulklike. Thus, our simulation elucidates the catalytic property of the atomic H. When H atoms are replaced by D atoms, atoms C_1 and C_2 in the original dimer are also separated and the D atom D_1 collided by C_n is no longer bonded to C_1 but to C_n instead. However, in this case C_n is not bonded at the C_1 - C_2 bridge site but is bonded at the site bridging C_1 and C_3 . At 249 fs, the speeds of C_n and D_1 are 0.0258 and 0.0755 Å/fs, respectively. They correspond to temperatures of 3.23×10^3 and 4.60×10^3 K or 0.278 and 0.397 eV. The transfer of kinetic energy from C_n to D_1 and the substrate is faster than the H case. However, C_n is not settled at the desirable C_1 - C_2 bridge site. These results show that the atomic mass plays an important role in crystal-growth dynamics.

The trajectories of C_n and the chemisorbed H atom and

the positions of neighboring atoms on C(111) after 593 fs of simulation are shown in Figs. 4(a)–4(c). In these figures, crosses 2, 4, 6, and 8 denote the positions of atoms initially in the first layer and crosses 1, 3, 5, and 7 are those initially in the second layer. Circles 1' to 8' show the positions of atoms 1 to 8, respectively, at 593 fs. Dashed arrows in Fig. 4(c) show that atoms 2, 5, 6, and 8 are displaced over distances greater than about 1 Å. In addition, atom 5 rises up from the second layer to the first layer, while atom 8 drops down from the first layer to the second layer. Nearest-neighbor bonds are shown in Fig. 4(c) by solid lines. Atoms 1', 3', 7', and 8' in the second layer are each bonded with one third-layer atom (not shown), two atoms in the same layer and one first-layer atom. C_n is bridge-bonded to atoms 2' and 4'. Atoms 2', 4', 5', and 6' in the first layer are bonded with only three C atoms as shown in Fig. 4(c). The local surface structure is drastically altered and the original π -bonded chain is broken. The H atom moves outward, so that it becomes bonded with C_n and is oriented toward the vacuum. The kinetic energies of C_n and H as functions of time are shown in Fig. 5. The amplitudes of oscillation of both kinetic energies increase after about 400 fs, which is due to the gain of energy associated with the change in the surface structure. At 593 fs, C_n and the H atom have speeds of 0.0187 and 0.117 Å/fs, respectively, which correspond to temperatures of 1.70×10^3 and 5.57×10^3 K or 0.146 and 0.480 eV, respectively. When a D atom replaces the H atom, the D atom is also freed from its original chemisorption site similar to the H case. However, in contrast to the H case the surface structure remains more or less Pandey's (2×1) π -bonded chain structure and C_n is bridge-bonded to atoms 4 and 8 in the π -bonded chain [shown by crosses in Fig. 4(c)]. At 348 fs, C_n and the D atom have speeds of 0.0299 and 0.0727 Å/fs, respectively. They correspond to temperatures of 4.34×10^3 and 4.27×10^3 K or 0.374 and 0.368 eV, respectively.

From the above results, one can deduce the following properties of the collision between gas-phase C atoms and the H and D atoms chemisorbed on diamond surfaces. When the gas-phase C atom approaches the chemisorbed H or D atom, it transfers a part of its kinetic energy to the H or D atom. Since H and D atoms are bonded to surface atoms, they cannot move freely downward when they are collided by the approaching C atom. The trajectories of C_n and the H atom shown in Figs. 2 and 4 suggest that the H atom shifts its bonding to C_n when C_n approaches it. Then C_n and the H atom move together like a diatomic molecule with C_n moving on the surface and with the H atom swinging rapidly on the vacuum side of C_n . This property is similar for the D atom. On the (100) surface, C_n settles quickly at the bridge site. On the (111) surface, C_n settles at a bridge site above the π -bonded chain when it collides with the D atom. When C_n collides with the H atom, it induces drastic alteration of the local surface structure. In this case, both C_n and the local surface structure do not settle even after 593 fs of simulation. Our simulation shows that the (2×1) π -bonded chain structure is unstable during the CVD diamond growth. The quick settlement of C_n on the (100) surface without migration over a long distance may be due to that C_n can form two bonds

with two surface atoms and a substantial part of its chemisorption-energy-converted kinetic energy can be transferred to the much lighter H or D atom. The shift of the bonding of the H or D atom to C_n can be attributed to the fact that the C atom tends to form four bonds. When the H or D atom is bonded to C_n instead of the surface atom, the surface benefits from forming two bonds between C_n and two surface atoms and from the reduction of the dangling bonds on C_n by the H or D atom.

In summary, based on our molecular-dynamics simulations we can deduce the following findings, which may help gain insight into the atomistic understanding of the role played by atomic hydrogen in diamond-film growth. First,

we find that the chemisorption-energy-converted kinetic energy of the incoming C atom can be effectively transferred to the much lighter hydrogen atom, so that the new carbon atom can quickly settle on the surface, except the H/C(111) case which induces drastic change of the surface structure. Second, due to the single covalent bonding and the strong C-H bonding nature the atomic H prefers to be bonded to an outermost C atom rather than to be bonded at the original chemisorption site and buried by the new C layer.

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