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Generation of 3D hydrocarbon thin films via organic molecular cluster collisions

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Abstract

Thin film growth through the consecutive impact of energetic ethyne molecular clusters with a non-rigid, hydrogen-terminated diamond (111) surface in vacuum has been studied using molecular dynamics simulations. A second-generation version of the reactive empirical bond-order potential for hydrocarbons developed by Brenner, that has been modified to include long-range van der Waals interactions, is used in the simulations. The velocities considered are in the hyperthermal region and are comparable with those that can trigger shock-induced chemistry in energetic materials. The resulting film structure is predicted to be significantly different from diamond, graphite, or diamond-like amorphous-carbon thin films. The evolving film morphology is discussed in detail and the results compared with single cluster impacts involving a comparable number of molecules. © 1998 Elsevier Science B.V.

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1. Introduction

There has been intense interest lately in new methods for growing high quality thin films with potential commercial applications. This is primarily due to the need for high-performance coatings on devices such as machine tools that are chemically inert, resistant to abrasion, easily cleaned, mechanically strong and stable at high temperatures [1]. Thin films can be produced by several methods, such as chemical vapor deposition [2], low-energy neutral-cluster beam deposition [3], laser plasma source techniques [4], ionized cluster beam deposition [5], and sputtering methods [6]. The resulting morphologies and structures of these

films vary widely, from single crystals to amorphous coatings to epitaxial films, depending on the process method and conditions. Film quality can be sufficiently controlled for technological applications, but a fundamental understanding of the deposition process and the properties of the resulting materials are significantly less advanced [3].

Molecular dynamics (MD) simulations of particle–solid surface impacts have been shown to be an effective way to provide detailed information about the atomic-scale processes taking place during the collisions and explicitly show the dependence of the processes on the reaction conditions. An area that has been the focus of much recent work is cluster–solid surface impacts, which appear to have unique phenomena associated with it not seen in single atom or ion–solid surface collisions. These unique characteristics are thought to be due

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to the temporary build-up of a high density of atoms or molecules and the deposition of significant amounts of energy in a very localized region of the surface.

Cluster–solid surface impacts have, therefore, been studied extensively using MD simulations. For example, the work of Shapiro and co-workers has yielded insight into the pathways used for the dissipation of excess internal energy following low-energy impact of gold clusters with rigid barriers and related the results to thin film applications [7]. Averback and co-workers [8,9] have investigated the effect of incident cluster kinetic energy and cluster size on the behavior of copper, nickel, and aluminum clusters following impact to determine under what conditions they form a “glob”, create surface creators, or spread epitaxially across the surface. In addition, Haberland et al. [10] have studied the way in which molybdenum thin film growth is affected by changes in the velocity of the impacting cluster. They have also explored the temperature and incident cluster kinetic energy conditions necessary for good thin film cohesion using both computational and experimental approaches [11]. They conclude that the MD simulations do offer a valid explanation of the experimentally observed film structure. Finally, Raz and Levine [12] have used a combination of MD simulations and experiments to examine the conditions under which an argon cluster shatters following impact with a surface. They find that fragmentation is reduced when there is no rapid thermalization following impact.

There have also been a few simulations that have focused on the impact of organic molecular species with a surface at hyperthermal velocities. For example, Raz and Levine have modeled the collision of a norbornadiene molecule embedded within a neon cluster with a surface at velocities of 6 km s^{-1} [13,14]. They find that the impact causes the norbornadiene to undergo a four-center reaction and rearrange to form the quadricyclane molecule. In addition, previous work by our group [15,16] examined the collision of single molecular clusters of ethyne, ethene and ethane with a clean diamond (111) surface. The simulations predicted that a significant number of addition reactions take place among the cluster molecules and

between the cluster molecules and surface atoms, with ethyne showing the most reactivity.

The ethyne cluster, which contained 64 molecules, was given an incident velocity of 12 km s^{-1} normal to the surface, which equals an external kinetic energy of $19.43 \text{ eV/molecule}$ (the binding energy of an ethyne molecule is 17.30 eV). By the end of the simulation, approximately 73% of the carbon atoms from the cluster had reacted to form linear, branched and networked chemical products, and the longest chain produced contained 12 carbon atoms. These chemical products can be thought of as very short polymer chains and may be classified as oligomers. Approximately 37% of these chemical products remained chemisorbed to the surface following impact, whereas the rest of the cluster scattered away from the surface. The products chemisorbed to the surface following the collision appeared to be the initial stages of thin film growth; however, the nucleation was too preliminary to allow for characterization of the film morphology.

There is some experimental evidence to support the results predicted in these simulations. Yamada and co-workers grew polyethylene thin films on glass and silicon substrates by ionized cluster beam deposition [5]. The resulting films closely resembled a single crystal of polyethylene at high ionization voltages, but had amorphous structure when deposited at thermal velocities. More recently, Garvey and co-workers [17] have used triple quadrupole mass spectrometry to observe ethene molecule polymerization when molecular clusters of these molecules impacted other molecular clusters in the gas phase. In addition, Aoki and co-workers [18] were able to produce solid state cross-linked polyacetylene using a diamond anvil cell at room temperature and high pressures, a process that has been modeled with first principles simulations by Bernasconi et al. [19]. Hence, it seems reasonable that a cluster–surface impact, with its high concentration of atoms and resulting increased temperatures and pressures, could lead to addition-reaction chemistry.

Most computational studies of cluster–solid surface collisions deal with the impact of a single cluster on a clean surface. While these provide important dynamical information about the pro-

cesses taking place on impact, they can only provide limited information about the morphology of the resulting thin film. Only a few studies have investigated the growth of a thin film through the impact of multiple clusters on a surface. For instance, Müller [20] performed an MD simulation of several clusters successively impinging on a perfect two-dimensional (2D) surface using a Lennard–Jones potential and monitored the evolving 2D film structure. These 2D simulations reflect many of the essential features of a full three-dimensional (3D) description of the impact process but they also restrict certain degrees of freedom of the interacting particles. Furthermore, the removal of the kinetic energy from a 2D cell is slower than from a 3D-cell [20], so thermal effects in the later stages of the simulation may affect film properties. Haberland et al. [10] studied the consecutive collision of Mo_{1043} clusters with an Mo(001) surface using the Finnis–Sinclair potential, and predicted the formation of a porous film at low cluster kinetic energy and a dense mirror-like film at higher cluster kinetic energy. Finally, Kelchner and DePristo have modeled homoepitaxy on Pd(001) and Cu(001) via low-energy deposition of 5-, 10- and 100-atom clusters [21]. They found that the resulting films have more 3D character than films grown via single-atom deposition at temperatures near 0 K.

This paper examines, through simulations, the growth of a 3D hydrocarbon thin film from the consecutive impact of energetic ethyne molecular clusters on non-rigid, hydrogen-terminated diamond (111) surfaces in a perfect vacuum (i.e. no oxygen present). Velocities of 12 km s^{-1} are used which are in the hyperthermal energy region and are comparable with the energies that can trigger shock-induced chemistry in energetic materials.

2. Computational details

The approach is MD simulations, where Newton's equations of motion are integrated with a third-order Nordsieck predictor corrector [22] to track the motion of all atoms with time, using a time step of 0.2 fs. The simulation conditions are

identical to those in Refs. [15,16] and only a brief summary will be provided here.

The MD approach is ideally suited to study cluster–solid surface collisions, as the time scales are on the order of a few picoseconds which is readily accessible using this technique. The forces on the individual atoms in both the clusters and surfaces were obtained from the same many-body reactive empirical bond-order (REBO) energy potential developed by Brenner and co-workers [23,24]. It allows bond formation and breaking to occur, the coordination of the carbon atoms to change, and it can characterize several thousand atoms on a standard workstation in a reasonable length of time. It also accurately reflects the energies, bond lengths, and lattice constants of both solid-state and gas-phase hydrocarbon materials, which is a crucial condition for these simulations.

The REBO potential is short-ranged, so long-range van der Waals or related forces have been added in the form of a Lennard–Jones (LJ) potential [22] that is non-zero only after the covalent energies have gone to zero (at about 2 \AA for carbon–carbon interactions); the LJ potential, therefore, models the intermolecular interactions within the molecular organic cluster.

The clusters examined are van der Waals clusters of ethyne which contain 64 molecules, or 256 atoms. Prior to impact, the 3D molecular clusters are equilibrated at 400–500 K and then cooled to 5 K to minimize the effect of internal cluster kinetic energy on the final results. The non-rigid, hydrogen-terminated diamond (111) surface is also equilibrated at 5 K and consists of 3136 atoms in 12 carbon layers, terminated by hydrogen layers on the top and bottom. The low equilibration temperature is used to minimize complications from thermal motion on the results of the cluster–surface collisions. The two layers on the bottom of the surface (one carbon and one hydrogen) are held rigid throughout the simulation. Moving towards the surface, three to four layers of carbon atoms have Langevin frictional forces [22] applied to maintain the temperature of the system and mimic the heat dissipation properties of a real diamond surface. The remaining atoms in the surface and all of the atoms in the cluster are allowed to evolve in time according to

Newton's equations of motion with no additional constraints.

3. Results

To investigate the effect of consecutive cluster impacts on the growth of the hydrocarbon thin film seen in previous simulations [15,16], we performed a series of simulations where ethyne molecular clusters impact a surface already covered with the chemical products of a single cluster–surface impact [15,16]. These simulations will therefore approximate consecutive impacts where the clusters collide with the surface several picoseconds apart and will show subsequent growth of the film that has already nucleated on the surface. Snapshots from a representative simulation are shown in Fig. 1. This simulation was performed three times from similar starting conditions. In each case the results were quantitatively similar.

At time $t=0.16$ ps, the surface has deformed elastically owing to the force of the impact and the cluster flattens and covers the existing film.

Most of the surface atoms return to their equilibrium positions, but the impact causes some of them to remain distorted. As the surface and cluster decompress from $t=0.30$ ps to $t=0.60$ ps, many of the cluster molecules scatter away from the surface, but there are also strong chemical reactions which take place among atoms in the cluster, film, and surface.

The simulations show that 48–56% of the carbon atoms from the cluster are involved in addition or polymerization reactions. The longest chain formed contains 17 carbon atoms where 35% of the atoms are from the cluster and 65% are from the original thin film. Several of the new chemical products scatter away from the surface, in some cases taking with them atoms that were part of the original thin film. There are also significant energy transfers which occur on impact that are very similar to those discussed in detail in [15,16]. Over 96% of the external cluster kinetic energy is transformed on impact into system potential energy (5%), cluster internal kinetic energy manifested in rotational and vibrational modes (19%) and surface kinetic energy (76%). The latter quan-

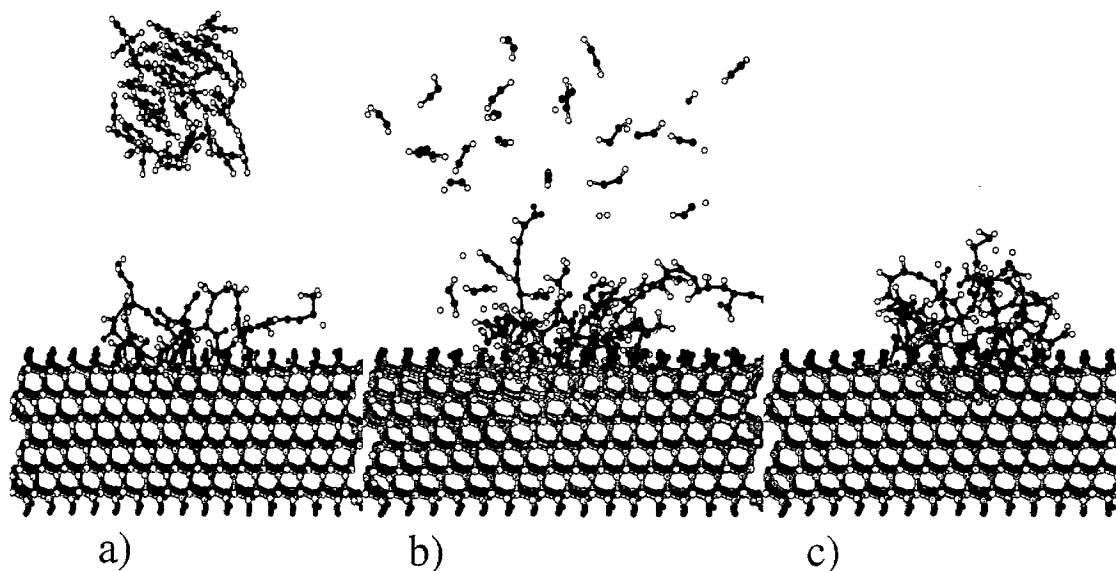


Fig. 1. Atomic positions from a representative trajectory of an ethyne molecular cluster impacting a diamond (111) surface covered with chemical products of a single cluster–surface impact with a velocity of 12 km s^{-1} at time: (a) $t=0.000$ ps, (b) $t=0.60$ ps, (c) $t=2.40$ ps. White spheres represent cluster hydrogen atoms, dark grey spheres represent hydrogen atoms terminating the diamond (111) surface, black spheres are cluster carbon atoms, gray spheres are carbon atoms of previously deposited films, and light gray spheres are surface carbon atoms.

tity is rapidly dissipated by the Langevin frictional forces in the surface (92% of the excess surface kinetic energy has been dissipated by $t=2.4$ ps) and does not affect the chemical reactions taking place at the surface.

At the end of the simulation, a new 3D thin film has been generated on the diamond (111) surface. The carbon in the new film came from the following sources: 46–53% of the atoms were part of the original thin film, 37–44% were from the cluster, and 10–12% were from the surface. Hydrogen makes up about 38–42% of the total film composition. Approximately 82–88% of the hydrogen atoms are from the impacting clusters, while the rest were originally terminating the diamond (111) surface.

Hence, the films contain a mixture of sp- (13–16%) and sp²-hybridized (84–87%) carbon atoms; this compares with crystalline diamond films which are purely sp³-coordinated, graphite which is purely sp²-hybridized and contains no hydrogen, or diamond-like amorphous-carbon films which contain a mixture of sp²- and sp³-hybridization [25]. The predicted films are also different from the solid state product in Ref. [19] which contained 22% sp-hybridized, 41% sp²-hybridized, and 37% sp³-hybridized carbon atoms. This film resembles a networked polymer thin film, but the networked chains are not large enough to be considered true polymers.

To determine the effect of elapsed time between cluster impacts, a second series of simulations was performed where two ethyne molecular clusters (each with the same size and velocity as the cluster discussed above), successively impact a clean, hydrogen-terminated diamond (111) surface within 0.03 ps of each other. Fig. 2 shows selected snapshots from a representative simulation of the collision process and the growth of the resulting thin film. Similar to the last set of simulations, this simulation was performed three times from the same starting conditions. In each case the results were quantitatively similar to the others, with value differences of less than 1%.

As expected, many polymerization reactions are again predicted to take place among the molecules within the two molecular clusters and between the clusters and surface. Overall, about 72% of the

carbon atoms in the clusters participate in chemical reactions. However, the location of the molecules within the clusters has a significant effect in determining whether or not a cluster molecule will react. For example, the molecules in the upper cluster (farthest from the surface) are less reactive than the molecules in the lower cluster (closest to the surface). Approximately 67% of the carbon atoms in the upper cluster react compared with about 75% of the carbon atoms in the lower cluster. The longest chain contains 21 carbon atoms, where 43% are from the upper cluster, 43% from the lower cluster and 14% are from the surface.

The energy transfers that take place are similar to those seen in the previous series of simulations, in that both clusters transform their external kinetic energy into other energy forms on impact. However, the process is significantly more complex. As the second cluster impacts, it not only converts about 96% of its external kinetic energy into system potential energy (20%), and surface kinetic energy (49%), it also transfers energy to the rebounding molecules of the first impacting cluster. Similarly, as the molecules in the first cluster rebound, they transfer energy to the molecules in the second impacting cluster. Altogether, about 32% of all the external cluster kinetic energy in the system is transferred into cluster internal kinetic energy. Once more, by $t=2.4$ ps, 92% of the excess surface kinetic energy has been dissipated by the Langevin frictional forces in the surface.

The resulting 3D thin films closely resemble the films grown in the previous set of simulations, with a few notable differences. These films are primarily composed of atoms from the lower cluster (45%) with the rest of the atoms coming from the upper cluster (25%) and the diamond (111) surface (30%). This represents a decrease in the percentage of atoms in the film of the first cluster and an increase in the percentage of atoms in the film from the surface compared with the first series of simulations. Again, the carbon atoms in the film are a mixture of sp- (17%) and sp²-hybridized (83%) carbon, and hydrogen makes up about 34% of the film, where 73% of the hydrogen atoms come from the clusters and 27%

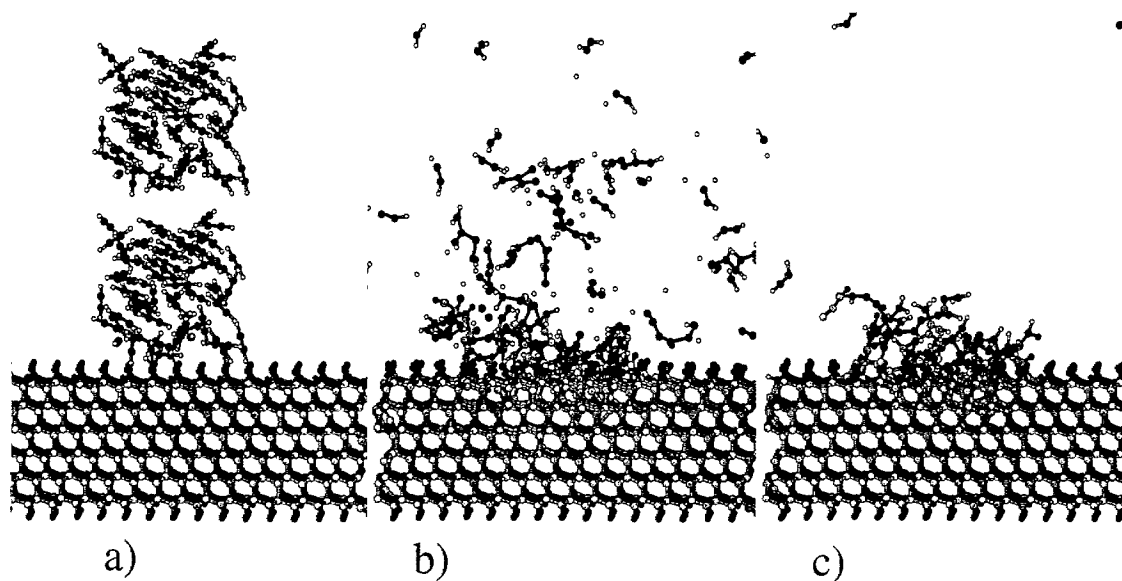


Fig. 2. Atomic positions from a representative trajectory of two ethyne molecular clusters consecutively impacting a clean diamond (111) surface with a velocity of 12 km s^{-1} at time: (a) $t=0.00 \text{ ps}$, (b) $t=0.60 \text{ ps}$, (c) $t=2.40 \text{ ps}$. Color designations are the same as in Fig. 1, except that here black spheres represent the upper cluster carbon atoms (farthest from the surface) and gray spheres represent the lower cluster carbon atoms (closest to the surface).

were originally terminating the diamond (111) surface.

4. Discussion

These 3D MD simulations provide important information regarding the details of thin film growth from consecutive organic molecular cluster–solid surface impacts. Both sets of collisions produce nearly identical 3D hydrocarbon thin films that show almost the same ratios of sp - and sp^2 -carbon hybridization and both contain about the same amount of hydrogen. However, the origin of the atoms that make up the films produced from the two processes is significantly different. When there is a long time between cluster impacts, the majority of carbon atoms in the film (90%) come from one of the two clusters and only about 10% are originally surface atoms. When the time between cluster impacts is very short, 71% of the atoms in the film come from the clusters with the rest coming from the surface.

This can be understood by examining the energy being transferred to the surface by these collisions. In the first case, each cluster contained a total of 1243 eV of incident kinetic energy that was allowed to fully dissipate before the next cluster impacted the surface. Thus, the surface atoms were less likely to be significantly perturbed and become incorporated into the film. However, when the time between impacts was short, the surface was not able to dissipate all of the energy from the first impact before the second cluster collided with the surface. Therefore, although each cluster contains about 1243 eV of incident kinetic energy, the surface feels about 2486 eV of energy. This causes surface atoms to become more disordered and to become incorporated into the thin film.

Secondly, the ratios of carbon atoms from the two clusters that make up the film are different. When the two clusters impact after a long time lag, each cluster contributes approximately equal numbers of carbon atoms to the film (the ratio varied from 1:1 to 1:4). However, when they impact with a short time lag, many more of the

carbon atoms in the film are from the lower cluster than are from the upper cluster (the ratio in all the simulations is about 1.8:1).

It is informative to compare the results of these consecutive cluster impacts with the results of impacting a single, larger molecular cluster of ethyne with a clean, hydrogen-terminated diamond (111) surface. The simulations discussed above involve a total of 128 molecules in two clusters impacting a diamond (111) surface at different times. We have previously examined the impact of a single cluster of 125 ethyne molecules with a clean hydrogen-terminated diamond (111) surface at the same velocity and reaction conditions [26]. More carbon atoms from the single 125-molecule reacted on impact, with about 78% of the atoms undergoing some kind of polymerization reaction. This is significantly more than the number of cluster atoms that reacted in the first series of simulations (48–56%) and slightly more than in the second series of simulations (75% and 67% for the first and second clusters respectively).

However, many more of the resulting chemical products scattered away from the surface, with only about 25% of the products remaining chemisorbed on the surface following impact (see Fig. 3). When the two smaller clusters impact consecutively with a long time lag, about 35% of all the resulting chemical products remain chemisorbed on the surface. This number drops to 26% of the total number of chemical products when the time lag between consecutive impacts is shortened to 0.03 ps. In short, the overall results indicate that when clusters consecutively impact a surface with short time lags between impacts, the reactivity of the clusters is similar to the reactivity of a single larger cluster. As the time lag between consecutive impacts increases, the overall reactivity of the clusters decreases but more of the chemical products remain chemisorbed to the surface following impact.

Examination of Fig. 3 also reveals that the structure of the film from the 125-molecule cluster impact covers a greater area but is not as thick, and is, therefore, more 2D than the films from the consecutive cluster impacts. It is about 43% hydrogen and is a mixture of sp -hybridized (46%) and sp^2 -hybridized (54%) carbon. Hence, the film

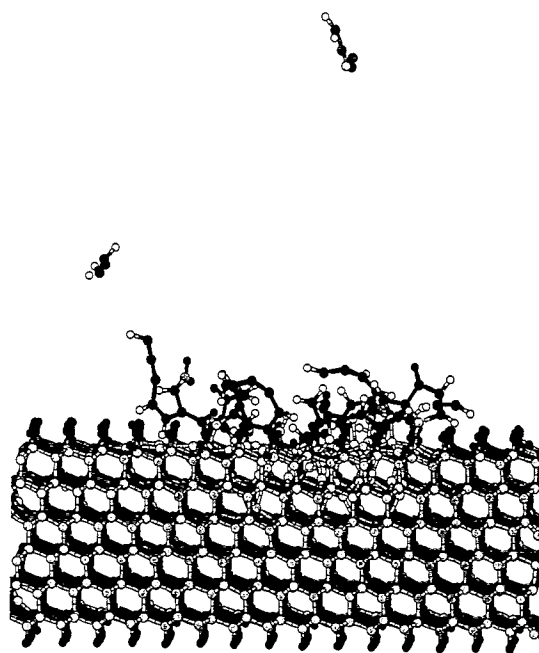


Fig. 3. Atomic positions at $t=2.40$ ps from a trajectory of an ethyne molecular clusters containing 125 molecules impacting a clean, hydrogen-terminated diamond (111) surface with a velocity of 12 km s^{-1} . Color designations are the same as in Fig. 1 except that here black spheres represent cluster carbon atoms in molecules in the upper half of the cluster and gray spheres represent cluster carbon atoms in molecules in the lower half of the cluster.

produced from a single larger cluster collision is significantly different from the film produced from consecutive cluster impacts. These differences are due to the larger number of molecule–molecule collisions (and hence chemical reactions) in the latter cases compared with a single, larger cluster–solid surface collision.

Finally, the simulations were carried out at a low starting temperature (5 K) for both the surface and the cluster to minimize complications from thermal vibrations and rotations on the results. Previous simulations of the impact of C_{60} with other C_{60} molecules [27] show that as the internal kinetic energy of the molecules increases, the amount of external energy needed for chemical reactions to occur decreases. However, the probability of a reaction taking place and the chemical products produced (two fused C_{60} molecules) depended only on the total energy in the system.

Analogously, it is expected that if the starting temperatures of the clusters and surface were higher, such as room temperature, the reactions predicted by these simulations would take place at lower impact velocities (or smaller external kinetic energies). Work is currently under way in our group to investigate the effects of surface temperature on the results.

5. Conclusions

The consecutive impact of ethyne molecular clusters with incident velocities of 12 km s^{-1} on hydrogen-terminated diamond (111) surfaces were studied using MD simulations. The consecutive impacts result in the growth of a 3D hydrocarbon thin film where the carbon atoms are primarily sp^2 -hybridized (over 80%) with some sp -bonding as well. A little over 30% of the film is composed of hydrogen. The film resembles a networked polymer structure, but the networked chains are not large enough to be classified as polymers. Therefore, these simulations suggest that a new type of amorphous hydrocarbon thin film might be created during hypervelocity impacts of molecular clusters with solid surfaces.

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