Polymerization via Cluster−Solid Surface Impacts: Molecular Dynamics Simulations

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Molecular dynamics simulations of collisions between simple organic molecular clusters and a nonrigid, hydrogen-terminated diamond (111) surface have been performed to study the chemical reactions that occur within the clusters and between the cluster and the surface as a result of impact. A second-generation version of the reactive empirical bond order potential for hydrocarbons developed by Brenner, which 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 to those that result in shock-induced chemistry in energetic materials and that occur between particles and solid surfaces in interstellar space. The outcome of the scattering event is monitored as the reactivity of the molecular cluster is varied, and the dependence of the chemistry on the incident cluster velocity and the position of the reacting molecules within the cluster is examined. We find that polymerization reactions occur when the incident cluster velocity corresponds to an external kinetic energy that is within 3 eV/molecule of the binding energy of an individual cluster molecule. Following impact, some of the chemical products chemisorb to the surface in the initial stages of thin film growth, but the exact nature of the thin film is not clear.

I. Introduction

Cluster impacts on solid surfaces are one of the most interesting topics in the area of particle−surface interactions. Cluster−surface collisions result in the deposition of significant amounts of energy in a very localized region of the surface accompanied by a transient and localized high density of atoms or molecules. This combination leads to expectations that these collisions will include collective phenomena not seen in individual atom− or molecule−surface collisions which have long been important in such processes as surface cleaning,[1] ion-implantation,[2] and chemical vapor deposition of thin films.[3] Some of the possible outcomes of cluster−surface impacts are scattering of cluster fragments, scattering of particles from the surface, chemical reactions between the cluster and the surface, chemical reactions within the cluster, and adhesion of the cluster to the surface.

There has been increased interest lately in cluster−surface collisions due to recent enhancements in cluster generators and laser vaporization sources.[4] Mahoney *et al.*[5] have used large cluster−surface impacts to sputter intact biomolecules from surfaces for analysis with mass spectrometry with relatively low chemical noise backgrounds. Tsukuda *et al.*[6] and Whetten and co-workers[7] have impacted carbon fluoride and sodium fluoride clusters on silicon surfaces and observed chemical reactions between fluorine and silicon at low cluster impact energies (0.1−0.5 eV/atom) and cluster fragmentation at higher impact energies. Researchers at the Universite Claude Bernard Lyon[8] have impacted free carbon clusters ranging from 20 to 900 atoms on several substrates at thermal velocities and generated carbon films approximately 100 nm thick. They find that there is a correlation between the properties of the clusters and the properties of the films created by impact, which can be diamond-like or graphite-like depending on the cluster size used. Finally, Thurner and co-workers[9] have found that the collision of metal clusters containing 1000 atoms and external kinetic energies of 5 eV/atom with metal substrates result in dense thin films

without columnar voids at room temperature. They have also found that cluster−surface impacts of ionized Cu clusters containing 1000−3000 atoms and energies of about 10 eV/atom can fill micrometer-sized contact holes on semiconductor devices.[10]

Some of these experiments have been motivated by intriguing results from atomistic simulations or have been modeled atomistically after the fact to better understand the experimental results. This is because simulations do not involve the technical challenges of the experiments, 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. For example, there has been much interest in the impact of metal clusters with solid surfaces. The work of Shapiro, Tombrello, 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.[11] They have also studied the mechanisms for atom ejection,[12] surface damage,[12] and core-excitation[12] following high-energy impacts (5−200 keV) of mixed gold and aluminum clusters on gold targets. Hsieh, Averback, and co-workers[13] 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 craters, or spread epitaxially across the surface. In addition, Haberland *et al.*[14] have studied the way in which molybdenum thin film growth is affected by changes in the velocity of the impacting cluster. Finally, Yamamura and Muramoto[15] have studied the depth profiles that result when silver clusters containing a few hundred atoms are bombarded on aluminum and silver targets with external kinetic energies of 200−400 eV/atom.

There has also been much interest in modeling the bombardment of solid surfaces with van der Waals clusters, such as argon. For example, simulations by Cleveland and Landman[16] have provided quantitative information about the buildup of density, temperature, and pressure within argon clusters during

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impact with sodium chloride surfaces and determined some of the mechanisms used to relieve these buildups. Tully and co-workers[17] have investigated the bombardment of platinum surfaces with argon clusters and determined the manner in which the fragmentation and scattering of the clusters depend on cluster size, incident cluster energy, and the angle of incidence of the cluster. Mayne and co-workers[18] have concentrated on the fragmentation of small argon and nitrogen clusters and documented the conditions under which portions of the initial cluster geometry survive the collision. Finally, Schek and Jortner[19] have observed microshock wave propagation in large argon clusters that bombard platinum surfaces at high energies.

Despite the impressive work in this area, there remain many unanswered questions. For example, few simulations have dealt with chemical reactions occurring between molecules within an impacting molecular cluster, especially organic molecular clusters. There is therefore much that is not known about the chemistry that occurs during such collisions, despite the fact that beams of simple organic molecules (such as methane and ethyne) and hydrogen are the starting materials in such important processes as the chemical vapor deposition of diamond films[20] and simple organic molecules are monomers in many widely used polymers such as polyethylene.

This paper examines the impact of molecular clusters of simple organic molecules on a hydrogen-terminated diamond (111) surface in vacuum (i.e., an oxygen-free atmosphere). The organic species considered are ethane, ethene, and ethyne, chosen because of their simplicity and the progressively decreasing bond saturation, and hence increasing reactivity, of the carbon atoms in each molecule. Velocities in the hyper-thermal energy region (corresponding to external kinetic energies of approximately 7−40 eV/molecule) are considered. The lower limit corresponds to a kinetic energy that can trigger shock-induced chemistry in energetic materials,[21] while the higher limit is the energy region most applicable to collisions of particles in interstellar space.[22] The size of the clusters (number of molecules) is held constant in this study. Preliminary results were reported in a recent publication.[23]

The first goal is to examine the chemical reactions that might occur following cluster impact with the surface as a function of reaction conditions. For example, the simulations can reveal the dependence of the final chemical products and intermediate states on an individual molecule's position within the molecular cluster. The second goal is to determine whether collisions of simple organic clusters with solid surfaces can be used to produce unusual intermediate states, perhaps ultimately leading to materials with unique, nonequilibrium structures and compositions. For example, the impact might produce high-energy intermediates that can be stabilized and used to make new materials. In addition, these high-energy collisions might overcome high activation barriers to produce chemical structures not usually reached through traditional synthetic channels.

The rest of the paper is organized as follows. Section II discusses the computational details of the potential used in the simulations and the manner in which the molecular clusters and the surfaces were constructed and equilibrated, while section III summarizes the simulation results. Section IV discusses the results and the effect of altering the simulation conditions. Finally, section V presents the conclusions.

II. Computational Details

The approach is molecular dynamics (MD) simulations, where Newton's equations of motion are integrated with a third-order Nordsieck predictor corrector to track the motion of the atoms with time.[24] A time step of 0.20 fs was used in all the simulations except where noted. This 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 through MD simulations. 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. It allows bond formation and breaking to occur and 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,[25] a crucial condition for these simulations.

The REBO potential has been successfully used to study a variety of processes involving both molecules and surfaces. For example, it has been used to study C_{60} collisions with other C_{60} molecules with external kinetic energies of 10−140 eV[26] and with hydrogen-terminated diamond (111) surfaces with external kinetic energies of 150−250 eV.[27] It has also been used to confirm the Eley−Rideal mechanism in the reaction of a phenathrene molecule with a chemisorbed benzene molecule.[28] In addition, it has been used to study many processes taking place on solid state carbon surfaces, such as tribochemistry at sliding diamond surfaces,[29,30] and nanometer-scale indentation and adhesion of diamond tips to diamond[31] and amorphous-carbon thin films.[32]

However, it yielded diamond elastic constants that were generally lower than experimental values. Hence, the REBO potential has been recently modified to accurately reproduce the elastic constants of diamond and graphite while maintaining its original properties.[33] The improved potential yields elastic constants for diamond of $c_{11} = 10.78 \times 10^{11}$ N m^{-2}, $c_{12} = 1.31 \times 10^{11}$ N m^{-2}, and $c_{44} = 6.8 \times 10^{11}$ N m^{-2}, which are in good agreement with the experimental values of $c_{11} = 10.76 \times 10^{11}$ N m^{-2}, $c_{12} = 1.25 \times 10^{11}$ N m^{-2}, and $c_{44} = 5.8 \times 10^{11}$ N m^{-2}.[34] It also includes improved analytic functions for the intramolecular interactions and an expanded fitting data base, which includes molecular bond energies, barriers for the formation of various radicals, and vibrational frequencies and heats of formation of many organic molecules. It has subsequently been used to study the patterning of diamond surfaces,[35] the ion bombardment of polymer surfaces with carbon and rare gas ions with energies of 20−80 eV/atom,[36] and the mechanical properties of amorphous-carbon thin films.[37]

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[24] that is nonzero only after the covalent energies have gone to zero (at about 2 Å for carbon−carbon interactions). The LJ potential therefore models the intermolecular interactions within the molecular organic cluster. While studies have shown that the behavior of van der Waals clusters depends strongly on the characteristics of the intermolecular potential for such processes as the H + CH_3 = CH_4 association reaction at room temperature,[38] cluster impact at hyperthermal velocities is expected to overwhelm the van der Waals forces holding the cluster together. Therefore, the results of the cluster−surface collisions should not be affected by small variations in the intermolecular LJ potential.

As is the case with most empirical potentials, there are instances when the REBO potential yields inaccurate results. For example, Hase and co-workers[39] have shown that the potential gives association rates for H + CH_3 and H + diamond (111) that are significantly smaller than experimental values. In addition, the electrons are not treated explicitly, so forces

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arising from effects such as orbital resonances and symmetry are not realistically treated.

The clusters examined are van der Waals clusters of ethane, ethene, and ethyne, and they impact the surface in an ideal vacuum. Each cluster contains 64 molecules, or 512 atoms in the ethane clusters, 384 atoms in the ethene clusters, and 256 atoms in the ethyne clusters. Prior to impact, the three-dimensional molecular clusters are constructed by replicating a single molecule on a regular three-dimensional grid, applying periodic boundary conditions to the system in three dimensions, and equilibrating at 400−500 K. Following equilibration, the clusters are cooled to 5 K to minimize the effect of internal cluster kinetic energy on the final results. Previous simulations of the impact of C_{60} with other C_{60} molecules[26] showed 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.

The nonrigid, 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 toward the surface, three to four layers of carbon atoms have Langevin frictional forces applied to maintain the temperature of the system and mimic the heat dissipation properties of a real diamond surface.[40] 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.

To simulate each cluster−solid surface collision, a series of trajectories were performed where the equilibrated cluster is positioned about 0.5 nm above the center of a clean, equilibrated surface and given an incident velocity normal to the surface. The system is then allowed to evolve in time as a result of the dynamics. Only collisions where the cluster impacts the surface along the surface normal are considered.

III. Results

III.A. Ethane Molecular Cluster Impact Results. The initial velocity considered for the ethane molecular clusters is 12 km/s, chosen because it is a hyperthermal velocity that corresponds to a cluster external kinetic energy of 22.41 eV/molecule, midway between the high and low external energy extremes under consideration. It is also close to the binding energy of ethane (29.41 eV/molecule). Figure 1 shows selected snapshots from a representative collision of the cluster with the hydrogen-terminated diamond (111) surface. When the cluster makes initial contact with the surface, it flattens out and the molecules impact each other in (mainly elastic) collisions. At time = 0.10 ps, the surface has elastically deformed to accommodate the force of impact, with maximum compression (about 1.5 Å displacement) occurring at time = 0.12 ps. From this point the surface returns to its original, preimpact position, the cluster begins to move away from the surface, and the cluster molecules begin to spread apart.

By the end of the simulation, the van der Waals bonds holding the cluster together have been broken and 25% of the covalent carbon−carbon (12% of the carbon−hydrogen) bonds within individual ethane molecules have broken. In the trajectory shown in Figure 1, a CH_3 fragment from an ethane molecule displaces a surface hydrogen atom and chemisorbs to the surface,

and several H_2 molecules are formed. This is typical of the level and type of chemical reactions observed.

To study the effect of incident kinetic energy on the collision outcome, the same cluster is given a velocity of 16 km/s normal to the surface, which corresponds to an external kinetic energy of 39.85 eV/molecule, at the high end of the range under consideration and significantly larger than the binding energy of an individual ethane molecule. Selected snapshots from a representative simulation are shown in Figure 2. Again, the impacting cluster flattens out on impact and causes the surface to deform by about 1.7 Å. Most of the surface atoms return to their equilibrium positions, but the impact is severe enough that some of them remain distorted (see Figure 2). In addition, as the cluster and surface decompress, between time = 0.30 ps and time = 0.60 ps, a significant number of chemical reactions take place between molecules in the cluster and between cluster and surface atoms.

Approximately 19% of the carbon atoms from the cluster are involved in addition reactions, which result in products that resemble very short polymers and may be considered to be oligomers Hence, the cluster−solid surface collision causes polymerization of the individual cluster molecules to take place in a manner not seen previously, but the products are too short to be considered true polymers. About 60% of these products remain chemisorbed to the surface at the end of the simulation, having displaced the surface hydrogen atoms at the chemisorption sites. The location of the molecules within the cluster relative to the surface, e.g., in the upper half (farthest from the surface) or in the lower half (closest to the surface), does not affect the probability of a molecule undergoing a chemical reactions (i.e., approximately equal numbers of molecules from the upper and lower halves of the cluster react). However, the majority of the atoms in the chemisorbed chemical products were originally in molecules in the lower half of the cluster.

Furthermore, about 40% of the atoms in the chemical products were originally surface atoms that were dislocated from the lattice as a result of the collision. The final chemical products range from dimers to chains that include up to six carbon atoms. The products that scatter away from the surface are 100% linear hydrocarbon chains, while those that remain on the surface are primarily linear, but some branching occurs as a result of chemisorption to the surface, as shown in Figure 2. In addition, several H_2 molecules are formed from hydrogen atoms knocked loose from impacting cluster molecules.

These simulations involve considerable transfer of energy, both within the incident cluster and between the cluster and the surface. When the ethane cluster impacts the surface with a velocity of 16 km/s, 92% of the cluster's external kinetic energy is converted to cluster internal kinetic energy manifested in rotational and vibrational modes (23%), system potential energy (18%), and surface kinetic energy (59%). Fully 88% of the excess surface kinetic energy is dissipated by the Langevin surface atoms by time = 1.2 ps, and over 95% of it is dissipated by time = 2.4 ps. Similar values are obtained for the ethane impact with a velocity of 12 km/s.

III.B. Ethene Molecular Cluster Impact Results. The second effect to be examined is carbon bond saturation within the cluster molecules. To facilitate this comparison, a cluster of ethene is given an incident velocity of 12 km/s, which equals an external kinetic energy of 20.92 eV/molecule (the binding energy of ethene is 23.55 eV). Numerous chemical reactions are observed between the molecules in the cluster following impact (see Figure 3). Unlike the collisions of the ethane clusters at a velocity of 16 km/s, however, these collisions do
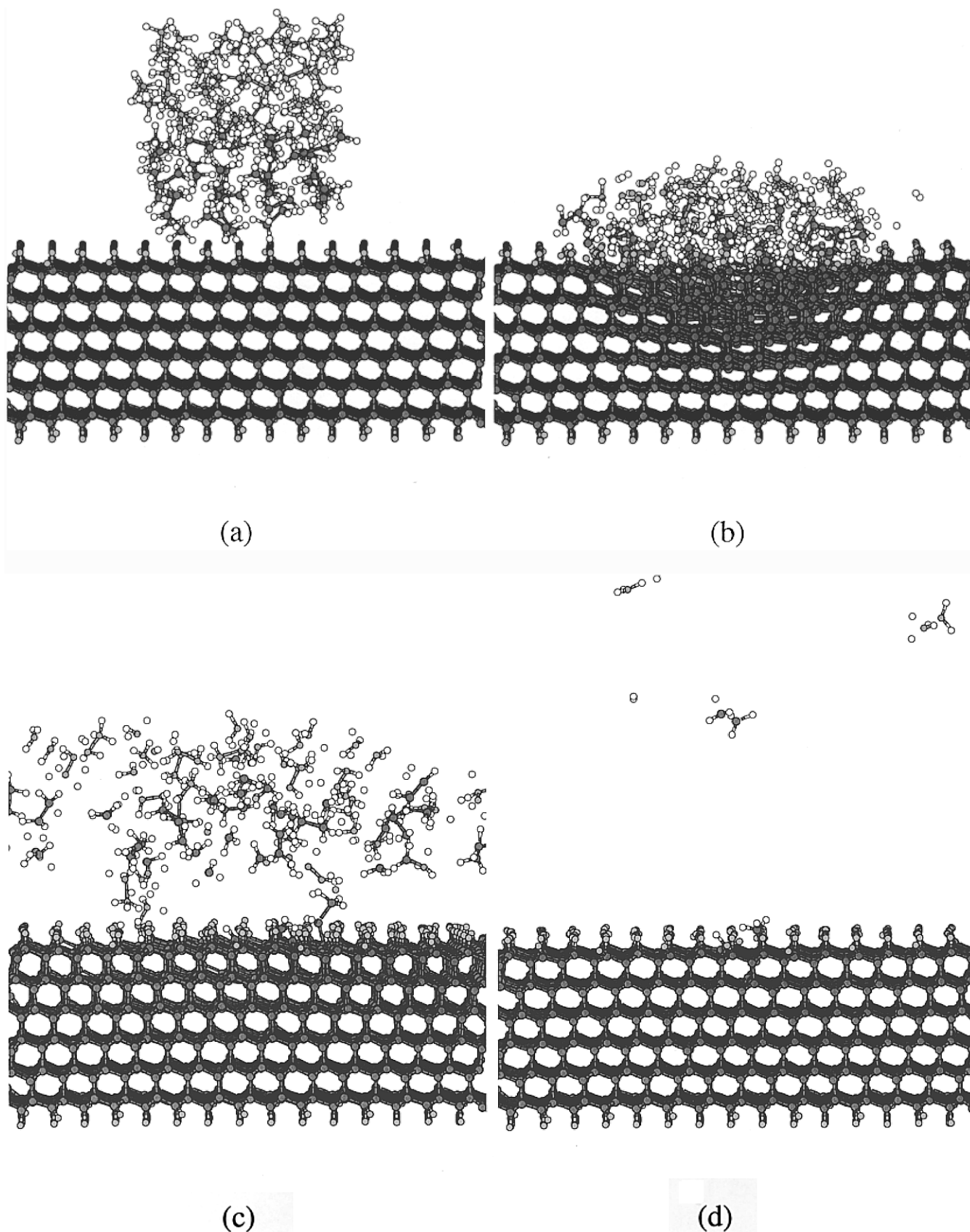
(a)

(b)

(c)

(d)

Figure 1. Atomic positions for a trajectory of an ethane molecular cluster impacting the surface with a velocity of 12 km/s at various times: (a) time = 0.00 ps, (b) time = 0.10 ps, (c) time = 0.30 ps, and (d) time = 1.20 ps. White spheres represent cluster hydrogen atoms, gold spheres represent hydrogen atoms terminating the diamond (111) surface, green spheres represent cluster carbon atoms in molecules in the lower half of the cluster, red spheres represent cluster carbon atoms in molecules in the upper half of the cluster, and gray spheres represent surface carbon atoms.

not result in any permanent surface disorder and the bonding arrangement between the carbon atoms in the diamond remains unchanged.

About 61% of the carbon atoms within the cluster undergo an intracluster chemical reaction leading to polymerization, with approximately 10% of the products chemisorbing to the surface.
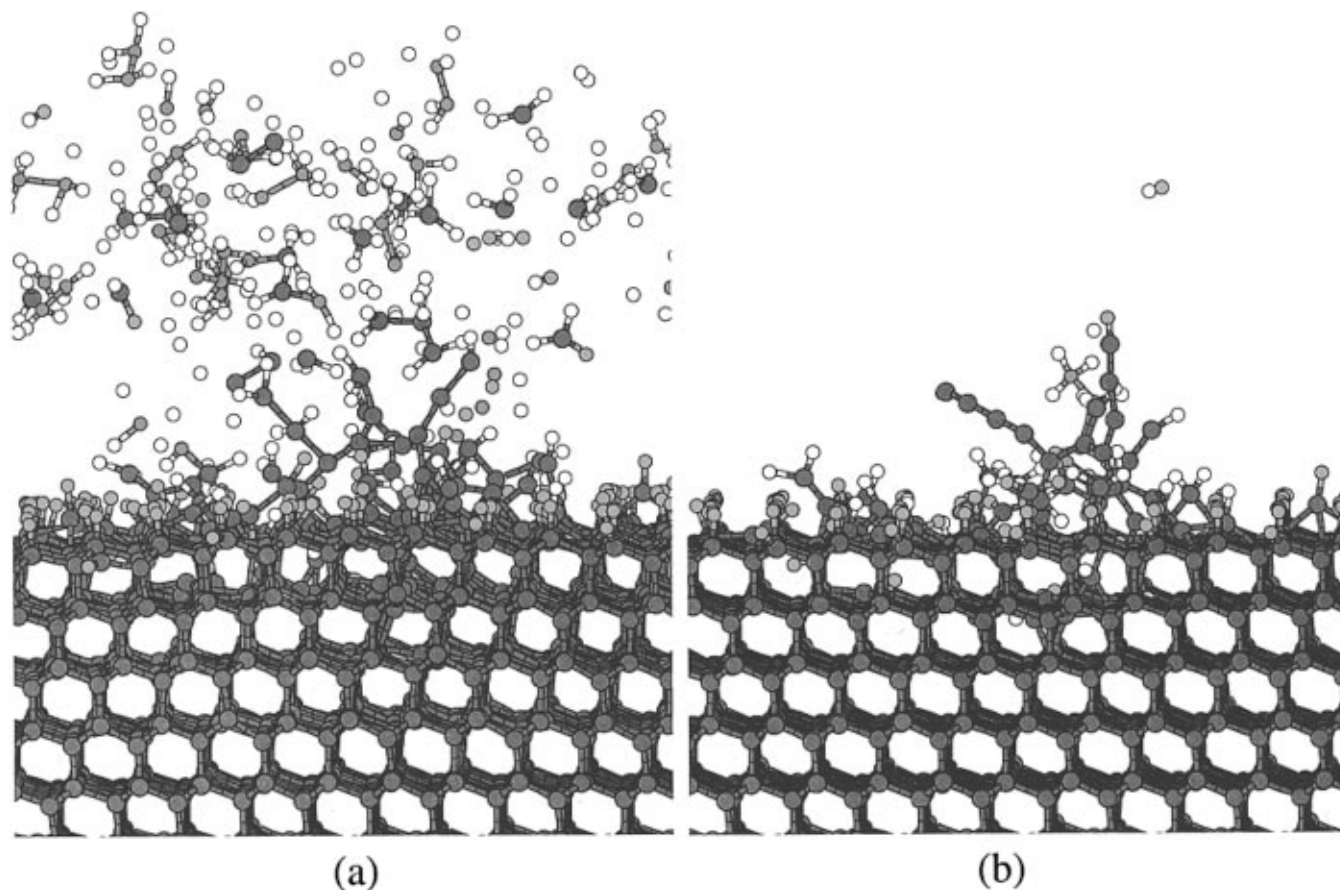
Figure 2. Atomic positions for a trajectory of an ethane molecular cluster impacting the surface with a velocity of 16 km/s at various times: (a) time = 0.30 ps and (b) time = 2.40 ps. Color designations are the same as in Figure 1.

The location of the molecules within the cluster relative to the surface plays a significant role in determining whether or not a cluster molecule will react. For example, most of the molecules in the lower half of the cluster react, while the 39% of the cluster molecules that do not react are mostly from the upper half of the cluster. In addition, all of the atoms in the chemisorbed molecular products were originally in molecules in the lower half of the cluster. Of the oligomer products produced, most are linear (74%) and the rest are branched (26%); the longest chain observed contained eight carbon atoms.

The energy transfers as a result of these collisions are as follows: 90% of the cluster external kinetic energy is transformed into cluster internal kinetic energy manifested in rotational and vibrational modes (25%), system potential energy (15%), and surface kinetic energy (60%). Of the excess surface kinetic energy, 88% is dissipated by the Langevin surface atoms by time = 1.2 ps, and 95% is dissipated by time = 2.4 ps.

When ethene clusters impact the diamond (111) surface with a velocity of 8 km/s (or an external kinetic energy of 9.30 eV/molecule which is near the lower energy limit under consideration here), mostly nonreactive, elastic collisions are observed, both between the individual cluster molecules and between the cluster molecules and the surface. The impact is strong enough to break the van der Waals bonds holding the molecular cluster together and scatter the molecules away from the surface, but is not enough to cause significant chemical reactions to occur within the cluster or between the cluster and the surface (an example of the type of reaction that is observed is the chemisorption of one CH_2 fragment to the surface).

III.C. Ethyne Molecular Cluster Impact Results. Ethyne is the most reactive molecular species considered so far and it is expected to undergo more additive chemical reactions

following solid surface impact than ethene for that reason. The cluster is given incident velocities of 12 km/s to start, which equals an external kinetic energy of 19.43 eV/molecule (the binding energy of an ethyne molecule is 17.30 eV). These impacts produce the largest number of observed polymerization reactions between the cluster molecules, with about 73% of the carbon atoms from the cluster reacting (see Figure 4). In addition, the collisions produce some atomic-scale surface disorder, with about 3% of the carbon atoms in the final reaction products starting out as surface atoms. Approximately 37% of the chemical products remain chemisorbed to the surface at the end of the simulation.

In addition, the higher reactivity of the molecular cluster species leads to the greatest observed variety of products: 53% are linear chains, 29% are branched chains, and 18% are networked structures. The longest observed chain contains 12 carbon atoms. The position of the molecules within the original cluster relative to the surface does not appear to play a significant role, as approximately equal numbers of lower and upper half molecules do not react at all.

The energy conversions as a result of these collisions are as follows: the external kinetic energy decreases by about 96% on impact as it is converted into cluster internal kinetic energy manifested in rotational and vibrational modes (about 20%), surface kinetic energy (about 72%), and system potential energy (about 8%). Of the extra surface kinetic energy, 81% of it is dissipated by the Langevin frictional forces in the surface by time = 1.2 ps, and 95% of it is dissipated by time = 3.0 ps.

However, when the cluster is given an incident velocity of 8 km/s (which corresponds to an incident kinetic energy of 8.63 eV/molecule), the results are very similar to those observed when ethene collides with the surface at this velocity.
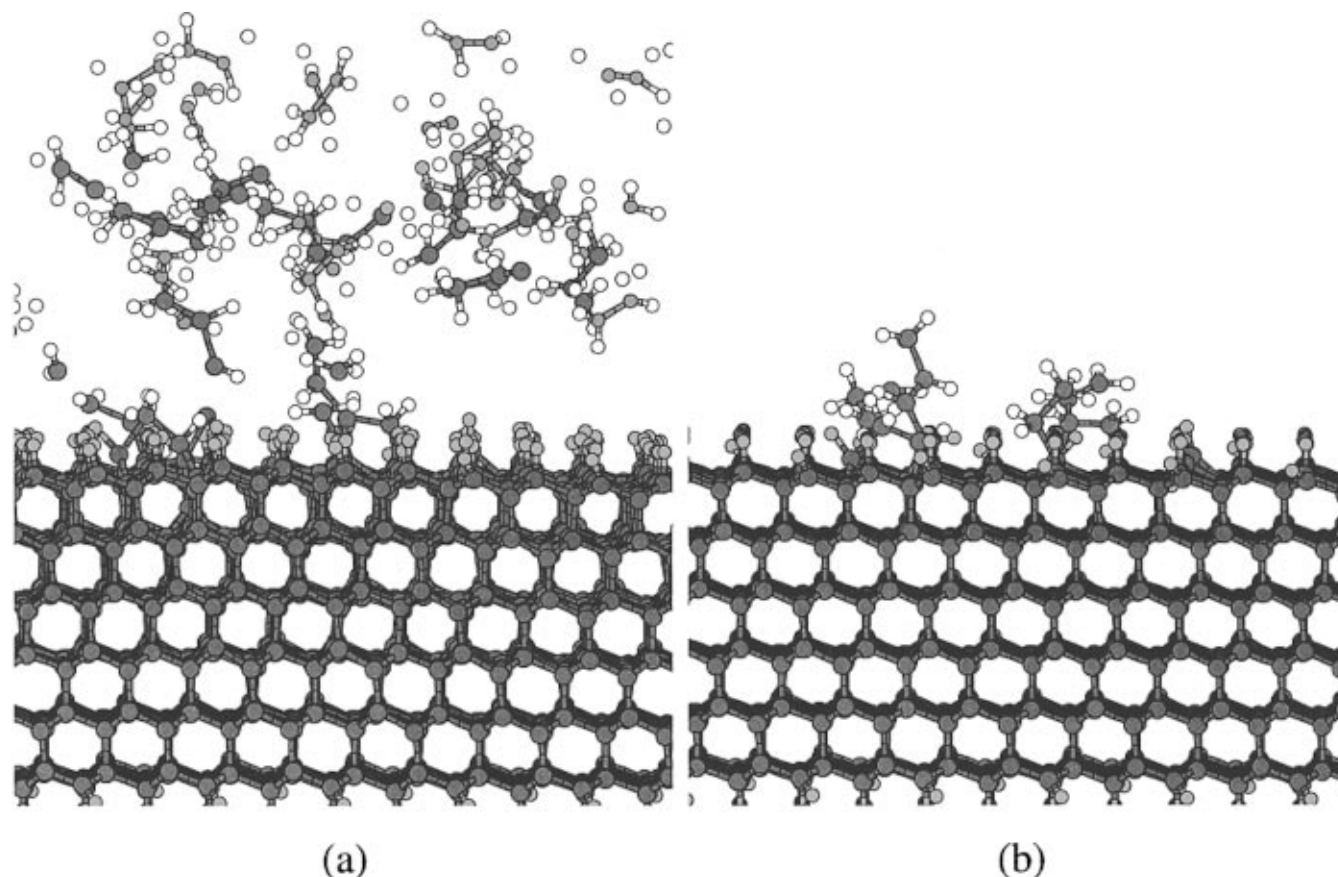
Figure 3. Atomic positions for a trajectory of an ethene molecular cluster impacting the surface with a velocity of 12 km/s at various times: (a) time = 0.30 ps and (b) time = 2.40 ps. Color designations are the same as in Figure 1.

IV. Discussion

To make absolutely sure that the excess kinetic energy pumped into the surface does not have a significant effect on the results, the simulations were repeated with different arrangements of Langevin and rigid atoms. First, a surface with the same Langevin and rigid atoms on the bottom of the surface was used with added Langevin atoms at the surface edges (about 3 Å from the edge of the substrate). The products of the cluster collisions with this new surface are identical to the products from the earlier simulations and the differences in the energy transfers are minimal (the ethyne cluster impacting at 12 km/s is a representative example: 94% of the external cluster kinetic energy is dissipated; 21% of it is converted into cluster internal kinetic energy, 8% is converted into system potential energy, and 71% is converted into surface kinetic energy; by time = 1.2 ps, 93% of the extra surface kinetic energy has been absorbed by the surface Langevin atoms, and that number has increased to 97% by time = 3.0).

Second, the simulations were repeated with the same Langevin atom configuration as in the original simulations, except that the formally rigid atoms on the bottom of the surface were changed to Langevin atoms and thus were not held rigid. The results of these simulations are again identical to those reported above except that the cluster transfers a small, finite amount of external kinetic energy to the surface on impact. Therefore, we feel confident that only minimal reflection of kinetic energy from the rigid layers occurs in the reported simulations.

Finally, the simulation of the ethyne cluster impact with a velocity of 12 km/s was repeated with no surface Langevin atoms to check energy conservation over the time lengths of the reported simulations. Energy is conserved to within 99.98% of the total energy, which is within acceptable limits.

In the reported simulations, numerous chemical and physical processes are taking place over very short time scales, which indicates that the results could be significantly affected by the time step used (too large of a time step might lead to incorrect results). Therefore, the simulation of the ethyne molecular cluster collision with a velocity of 12 km/s was repeated with a smaller time step of 0.15 fs and a larger time step of 0.30 fs. These simulations produced minimal (approximately 1%) quantitative differences in the percentage of cluster molecules that react.

Thus, we feel confident that the reported simulations are accurate within the constraints of the potential discussed above.

Several important trends are apparent from the results. The first is that the cluster's incident kinetic energy has a significant effect on the results of cluster−surface impact. No significant chemical reactions result if the external kinetic energy is less than about 3 eV/molecule below the binding energy of a single cluster molecule. For collision energies greater than this value, intracluster additive chemical reactions take place on impact and lead to oligomer products.

Secondly, the overall reactivity of the cluster (due to either (1) external kinetic energies per molecule that are significantly higher than the molecular binding energies or (2) unsaturated carbon atoms in the molecules) determines whether the collision causes atomic-scale surface disorder. Higher overall cluster reactivities lead to more surface atoms reacting and more surface disorder. The overall reactivity of the cluster also affects whether the position of the molecules in the cluster relative to the surface affects the results. The higher the overall reactivity, the less it matters where the molecules are in the cluster.

Finally, the products of the cluster−surface impact depend significantly on the reactivity of the individual cluster molecules,
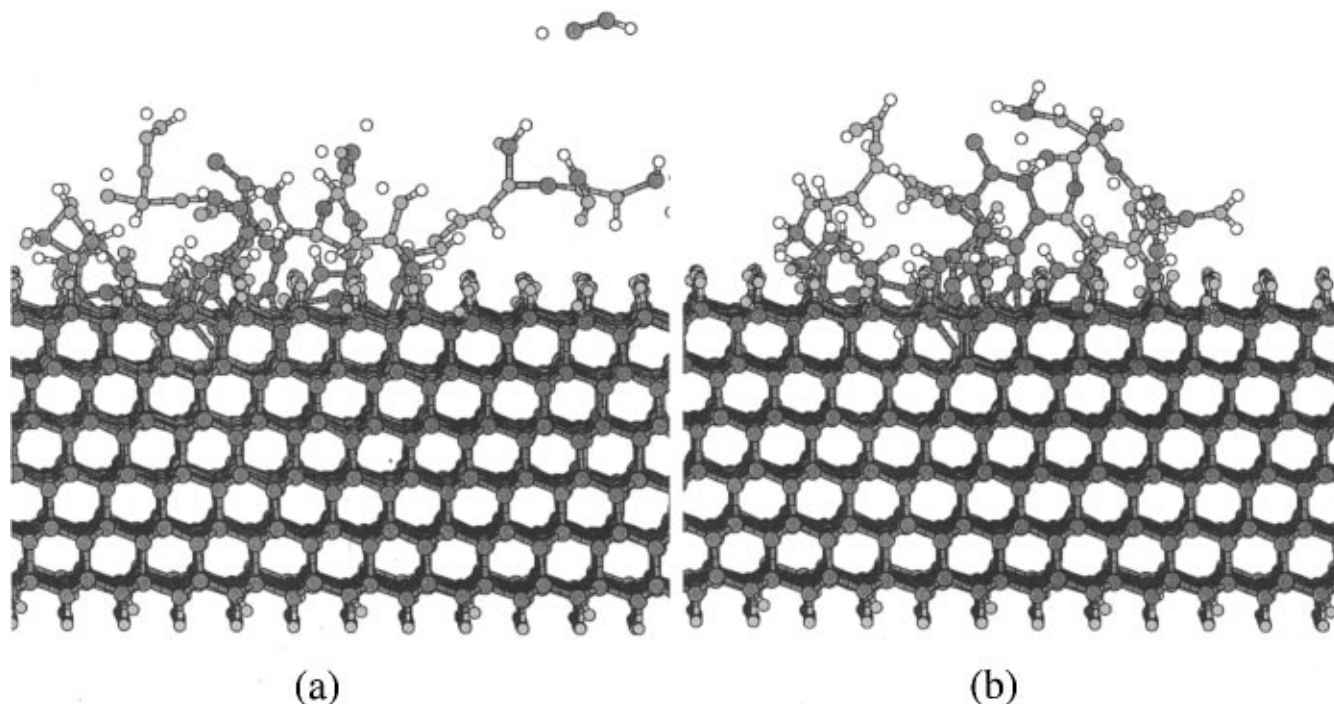
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Figure 4. Atomic positions for a trajectory of an ethyne molecular cluster impacting the surface with a velocity of 12 km/s at various times: (a) time = 1.20 ps and (b) time = 3.00 ps. Color designations are the same as in Figure 1.

with the less reactive molecules producing mainly linear chains and the degree of cross-linking increasing with increasing reactivity. Moreover, as the overall reactivity of the cluster increases, the percentage of the products sticking to the surface increases. The chemical products that remain chemisorbed to the surface following impact may be thought of as the nucleation of a hydrocarbon film on the diamond (111) surface, but the exact nature of the film is not clear (amorphous-carbon, polymer, or something new).

These trends are consistent with the results of earlier simulations of the collision of C_{60} with hydrogen-terminated diamond (111) surfaces.[27] These simulations showed that when C_{60} impacted the surface with external kinetic energies of 150 eV, the surface deformed elastically before the molecule scattered away in a nonreactive collision. As the external kinetic energy of the C_{60} increased, however, the probability of chemical reactions with the surface increased. For example, at kinetic energies of 250 eV, chemical reactions occurred 72% of the time where the molecule either chemisorbed to the surface, abstracted a hydrogen atom from the surface, or left a molecular fragment chemisorbed on the surface.

In this study, comparable chemical reactions (e.g., breaking a small number of covalent carbon−carbon bonds, chemisorption of a cluster molecule or molecular fragment to the surface) occurred[41] only for ethene and ethyne clusters at external kinetic energies about twice as big as in the C_{60} collision simulations (about 8 eV/molecule or 512 eV/cluster) and about 6 times as big for ethane clusters (about 22 eV/molecule or 1408 eV/cluster). The high value for the ethane molecular clusters is primarily due to the high stability of ethane relative to the other considered molecules. In addition, all the van der Waals clusters

are able to transform their incident kinetic energy into internal kinetic energy through intermolecular elastic collisions, a mechanism not available to the impacting C_{60} molecules. Finally, the C_{60} molecules were equilibrated at 300 K prior to impact in contrast to the much colder van der Waals cluster molecules considered here. Simulations are currently underway to quantify temperature effects on the observed chemical reactions.

V. Conclusions

Molecular dynamics simulations of the collision of molecular clusters of simple organic molecules with nonrigid, hydrogen-terminated diamond (111) surfaces have been performed. As a result of impact at hyperthermal velocities between 20 and 40 eV/molecule, the molecules in the cluster react with each other and the surface to form linear, branched, and networked oligomers. In addition, some of the chemical products remain chemisorbed to the surface following impact in the initial stages of film growth, where the nucleation is too preliminary to allow for characterization of the film morphology.

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