

# Atomistic simulations of organic thin film deposition through hyperthermal cluster impacts

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Atomistic simulations have been used to study thin film growth through the impact of energetic acetylene molecular clusters with three nonrigid, diamond (111) surfaces in vacuum. The surfaces considered include clean, bare-carbon diamond (111), clean hydrogen-terminated diamond (111), and hydrogen-terminated diamond (111) partially covered by a hydrocarbon film. The velocities considered are in the hyperthermal region (corresponding to external kinetic energies of about 20 eV/molecule) and are comparable to those that can trigger shock-induced chemistry in energetic materials. The collision caused the molecules in the cluster to undergo addition chemistry with other cluster molecules and/or with the surface resulting in thin film growth. We discuss the effect of surface reactivity on the products of the collision, including the resulting thin film morphology. © 1998 American Vacuum Society. [S0734-2101(98)02203-9]

## I. INTRODUCTION

Particle-surface interactions are important for numerous processes including surface structure determination, ion implantation, surface sputtering, and thin film growth.<sup>1</sup> Atomistic simulations of particle–solid surface impacts have been shown to be an effective way of providing detailed information about the atomic-scale processes taking place during impact and explicitly show the dependence of the processes on the reaction conditions. One area that has been the focus of much recent work is cluster–solid surface impacts. Such collisions have unique characteristics thought to be due to the temporary buildup 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 collisions have therefore been extensively studied using atomistic simulations. Most of these have focused on metal<sup>2–7</sup> or noble gas<sup>8–12</sup> cluster impacts but there have also been a few simulations that have focused on the impact of organic molecular species with surfaces at hyperthermal velocities. For example, Raz and Levine have modeled the collision of a norbornadiene molecule embedded in neon at velocities of 6 km/s.<sup>13</sup> They find that the impact causes the norbornadiene to undergo a four-center reaction and rearrange to form the quadricyclane molecule. Previous work by our group<sup>14</sup> examined the collision of single molecular clusters of acetylene, ethylene, and ethane with a clean, hydrogen-terminated 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 acetylene showing the most reactivity. We have also examined the effect of incident kinetic energy and cluster size on the results<sup>15</sup> and considered the consecutive impact of acetylene clusters with a hydrogen-terminated diamond (111)

surface.<sup>16</sup> The consecutive impacts resulted in the growth of a three-dimensional hydrocarbon thin film where the carbon atoms were primarily  $sp^2$  hybridized (over 80%) with some  $sp$  bonding as well. A little over 30% of the film was composed of hydrogen and it resembled a networked structure of short polymers (oligomers).

There is some experimental evidence to support the results predicted in Refs. 14–16. Garvey and co-workers<sup>17</sup> used triple quadrupole mass spectrometry to observe ethylene molecule polymerization when molecular clusters of these molecules impacted other molecular clusters in the gas phase. Aoki and co-workers<sup>18</sup> produced solid state crosslinked 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.*<sup>19</sup> More directly, ionized cluster beam deposition<sup>20,21</sup> has been used to grow thin films of anthracene, polyethylene, and phthalocyanine on silicon and glass substrates. It was found that at thermal velocities amorphous polymer films formed whereas at external kinetic energies of several keV, the process produced crystalline polymer films.

This article examines, through simulations, the impact of small clusters of acetylene with a clean, bare-carbon diamond (111) surface (i.e., an activated diamond surface with no hydrogen termination). The clusters impact the surface with velocities of 12 km/s, which are in the hyperthermal energy region and correspond to external kinetic energies of nearly 20 eV/molecule. These external energies are comparable to the energies that can trigger shock-induced chemistry in energetic materials. The results are compared to acetylene cluster collisions under similar conditions with diamond surfaces that are hydrogen-terminated and partially covered with a hydrocarbon thin film.

## II. COMPUTATIONAL DETAILS

The atomistic approach used is the molecular dynamics (MD) method using a third-order Nordsieck predictor

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corrector<sup>22</sup> with a time step of 0.2 fs. 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.<sup>23</sup> 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.

As is the case with most empirical potentials, there are instances when the REBO potential yields inaccurate results. For example, it has been shown<sup>24</sup> that the potential gives association rates for H+CH<sub>3</sub> and H+diamond (111) that are significantly smaller than experimental values. In addition, the electrons are not treated explicitly so forces arising from effects such as orbital resonances and symmetry are not realistically treated.

However, it has been successfully used to study a variety of processes involving both molecules and surfaces in addition to those mentioned in Refs. 14–16. For example, it has been used to study C<sub>60</sub> collisions with other C<sub>60</sub> molecules with external kinetic energies of 10–140 eV<sup>25</sup> and with hydrogen-terminated, diamond(111) surfaces with external kinetic energies of 150–250 eV.<sup>26</sup> It has also been used to confirm the Eley–Rideal mechanism in the reaction of a phenanthrene molecule with a chemisorbed benzene molecule<sup>27</sup> and to study many processes taking place on solid state carbon surfaces, such as tribochemistry at sliding diamond surfaces.<sup>28</sup>

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<sup>22</sup> that is nonzero only after the covalent energies have gone to zero (at about two Angstroms for carbon–carbon interactions). The LJ potential therefore models the intermolecular interactions within the molecular (van der Waals) organic cluster. For complete potential details please see the Appendix in Ref. 29.

The clusters considered in this work contain 64 acetylene molecules, or 256 atoms. Prior to impact, they 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 clusters are rapidly quenched, so the resulting cluster has an amorphous morphology. This is in contrast to other MD simulations that focused on studying low-temperature, ordered crystalline phases of acetylene.<sup>30</sup> The nonrigid surface consists of 3136 atoms in 12 carbon layers and is also equilibrated at 5 K. The bottom layer of the surface (furthest from the cluster) is hydrogen-terminated and is held rigid throughout the simulation. Moving towards the surface, three-four layers of carbon atoms have Langevin frictional forces<sup>22</sup> 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.

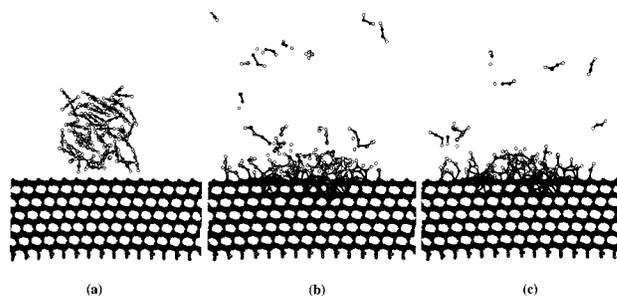


FIG. 1. Atomic positions from the trajectory where the acetylene molecular cluster impacted a bare, diamond (111) surface with a velocity of 12 km/s at times: (a) time=0.00 ps; (b) time=0.60 ps; (c) time=2.40 ps. The color designations are as follows: white spheres represent cluster hydrogen atoms; black spheres are cluster carbon atoms in the upper half of the cluster; light gray spheres are carbon atoms in the lower half of the cluster; gray spheres are surface carbon atoms.

### III. RESULTS

To investigate the effect of surface reactivity on the chemical products of an acetylene cluster-diamond collision, we performed a simulation where the cluster impacted a diamond (111) surface from which the surface hydrogen had been removed (see Fig. 1). The cluster had a velocity of 12 km/s (external kinetic energy of about 20 eV/molecule). These conditions are similar to those used previously to impact acetylene clusters on hydrogen-terminated diamond (111)<sup>14</sup> and a diamond surface covered by an acetylene thin film.<sup>16</sup>

At time=0.16 ps, the surface has deformed elastically due to the force of the impact and the cluster flattens. Most of the surface atoms return to their equilibrium positions but the impact causes some of them to remain distorted. From time=0.30 ps to time=0.60 ps, many of the cluster molecules scatter away from the surface but there are also strong chemical reactions that take place among atoms in the cluster, film, and surface during the time that the cluster is flattened on the surface.

The simulation shows that about 72% of the carbon atoms from the cluster are involved in addition reactions (the longest chain formed contained 14 carbon atoms). About 50% of the cluster carbon atoms remain chemisorbed to the reactive diamond surface in the start of a thin film. The carbon atoms in the film came from the following sources: 82% are from the cluster (13% from the upper half of the cluster, 69% from the lower half of the cluster) and 18% of the atoms are from the surface. Hydrogen makes up about 38% of the total film composition. The film is relatively dispersed over the surface and most of the longer chains scatter back into vacuum following impact.

Hence, the film contains a mixture of *sp* (21%) and *sp*<sup>2</sup> (79%) hybridized carbon atoms, in contrast to crystalline diamond films that are purely *sp*<sup>3</sup> coordinated, graphite that is purely *sp*<sup>2</sup> hybridized and contains no hydrogen, or diamondlike, amorphous carbon films that contain a mixture of

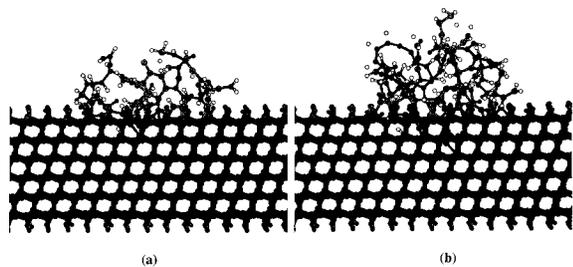


FIG. 2. (a) Atomic position at time=3.00 ps from a representative trajectory of an acetylene molecular cluster impacting a clean, hydrogen-terminated diamond (111) surface with a velocity of 12 km/s. (b) Atomic position at time=2.40 ps from a representative trajectory of an acetylene molecular cluster impacting a hydrogen-terminated diamond (111) surface already covered with a thin film of acetylene with a velocity of 12 km/s. Color designations in (a) and (b) are the same as in Fig. 1.

$sp^2$  and  $sp^3$  hybridization.<sup>31</sup> The predicted films are also different from the solid state product in Ref. 19 that contained 22%  $sp$  hybridized, 41%  $sp^2$  hybridized, and 37%  $sp^3$  hybridized carbon atoms.

There are also significant energy transfers that occur on impact that are very similar to those discussed in detail in Refs. 14–16. 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 quantity is rapidly dissipated by the Langevin frictional forces in the surface (92% of the excess surface kinetic energy has been dissipated by time=2.4 ps) and does not affect the chemical reactions taking place at the surface.

#### IV. DISCUSSION AND CONCLUSIONS

All the simulations discussed above were carried out at a low starting temperature (5 K) to minimize complications from thermal vibrations and rotations on the results. Previous simulations of the impact of  $C_{60}$  with other  $C_{60}$  molecules<sup>32</sup> 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. 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 slightly lower impact velocities (or

external kinetic energies). Work is currently underway in our group to investigate the effects of surface temperature on the results.

These results show many similarities to the data from two previous sets of simulations<sup>33</sup> where similar acetylene clusters impacted (1) clean hydrogen-terminated diamond (111) surfaces [see Fig. 2(a)] and (2) surfaces already covered with the start of a thin film [see Fig. 2(b)]. A comparison of the results is presented in Table I. The table shows that similar thin film structures result when the molecular acetylene clusters impact clean diamond (111) surfaces, irrespective of the identity of the terminating atoms. In addition, similar numbers of cluster atoms polymerize and remain chemisorbed to the surface on impact for each of the clean surface cases.

However, there are a few differences in the results for the two clean diamond surfaces. For example, in the case of a clean, bare-carbon diamond (111) surface, the film is composed of generally shorter chains and is relatively two-dimensional with a thickness of 4.7 Å. The film becomes more three-dimensional when the surface is hydrogen terminated, with a greater thickness of 7.6 Å. This is because the molecules do not adhere as rapidly in the latter case and hence have opportunities to react both on their way down and when they scatter back up into vacuum.

The collision results change more significantly when the cluster impacts a surface already partially covered with a thin acetylene film. The new film that results from the impact is again three-dimensional (average thickness is about 8.7 Å) but many fewer cluster molecules react on impact or stick to the surface following the collision. This is because there are opportunities for energy to be transferred to the thin film as internal kinetic energy in addition to the pathways that lead to chemical reactions (as discussed in Ref. 16). This result agrees with the findings of Hanley and co-workers<sup>34,35</sup> who have studied the energy transfers that take place when  $C_4H_4S^+$ ,  $Si(CD_3)_3^+$ , and  $Fe(C_2H_5)_2^+$  are scattered from clean and hexanethiolate covered Au (111) surfaces at incident energies of 10–70 eV/molecule. Their simulations showed that the surfaces covered by organic monolayers had more efficient energy transfers than the clean Au surfaces. Hence, even though the thin film partially covering the surface at the start of the simulation grows following the cluster collision, this surface is less reactive than the two clean surfaces.

In short, these simulations predict that thin organic films

TABLE I. Summary of results for impacts of acetylene molecular clusters with diamond (111) surfaces terminated as indicated.

Surface termination prior to cluster impact	% Cluster molecules reacted	% Cluster molecules that form film	Final film composition (source of C atoms)	Hybridization of C atoms in the film	% H in the film
Bare diamond (111)	72%	50%	82% from cluster 18% from surface	21% $sp$ hybridized 79% $sp^2$ hybridized	38%
H-terminated diamond (111)	70%–73%	46%	90% from cluster 10% from surface	30% $sp$ hybridized 70% $sp^2$ hybridized	38%
Diamond (111) covered with acetylene thin film	48%–56%	27%–37%	37%–44% from cluster 46%–53% from thin film 10%–12% from surface	13%–16% $sp$ hybridized 84%–87% $sp^2$ hybridized	38%–42%

can be grown through collisions of molecular organic clusters at hyperthermal velocities of about 20 eV/molecule with rigid, unreactive surfaces, such as diamond, and that the termination of the substrate is relatively unimportant to the process.

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