

Hydrocarbon thin films produced from adamantane–diamond surface deposition: Molecular dynamics simulations

Thomas A. Plaisted^{a)} and Susan B. Sinnott^{b)}

Department of Chemical and Materials Engineering, The University of Kentucky,
Lexington, Kentucky 40506-0046

(Received 25 August 2000; accepted 30 October 2000)

Atomistic simulations are used to study thin-film growth through the deposition of beams of adamantane molecules on hydrogen-terminated diamond (111) surfaces. A range of incident velocities from 13 to 17 km/s (corresponding to kinetic energies of 119–204 eV/molecule) are considered that fall in the hyperthermal energy region for particle deposition on surfaces. The forces on the atoms in the simulations are calculated using a many-body reactive empirical potential for hydrocarbons. During the deposition process the adamantane molecules react with one another and the surface to form hydrocarbon thin films that are primarily polymeric with the amount of adhesion depending strongly on incident energy. Despite the fact that the carbon atoms in the adamantane molecules are fully sp^3 hybridized, the films contain primarily sp^2 hybridized carbon with the percentage of sp^2 hybridization increasing as the incident velocity goes up. These results are compared with the predictions of simulations that examine the deposition of ethylene molecular and cluster beams. © 2001 American Vacuum Society. [DOI: 10.1116/1.1335683]

I. INTRODUCTION

Over the last few years, the controlled deposition of hydrocarbon thin films has been the focus of much study as researchers have grown various types of amorphous carbon, diamond, and polymeric structures through such methods as mass selected ion beams,^{1–4} chemical vapor deposition,^{5,6} and cluster-beam deposition.^{7–9} These studies have demonstrated how changes in the deposition method, starting material, and reaction conditions influence the final product. However, despite these advances there is still much that is not known about the atomic reactions that lead to thin-film nucleation and growth. Several groups have therefore employed advanced computational modeling methods to shed light on the fundamental physical and chemical processes that lead to thin-film development.^{10–12} We have previously studied the generation of polymeric thin films that are strongly adhering to the underlying diamond substrate through ethane, ethylene, and acetylene molecular and cluster-beam deposition.¹³ This work has shown how molecular reactivity,¹⁴ surface reactivity,¹⁵ incident velocity,¹³ and cluster size¹⁶ influence the nucleation, growth, and structure of the resulting thin films.

In this article we report the results of simulations where adamantane molecular beams are impacted on hydrogen-terminated diamond (111) substrates. The motivation for this work is the desire to explore the possible generation of diamondlike structures by depositing a starting material that has a configuration similar to that of diamond. The approach used in the study is classical molecular dynamics simulations. The dependence of the results on the incident velocity

of the molecules in the beam is also investigated. Previous studies of ethylene molecular and cluster-beam deposition showed a significant increase in film adhesion as the impact velocity increased from 13 to 18 km/s¹⁷ in agreement with experimental deposition studies of polyethylene on various substrates.⁴ Therefore we have further investigated this range of velocities with adamantane molecular beams to facilitate a qualitative comparison with the ethylene deposition results and to determine if there is a critical velocity above which film adhesion greatly improves.

II. COMPUTATIONAL DETAILS

The forces on all the atoms in the simulations are calculated using the reactive empirical bond order potential¹⁸ coupled to long-range carbon–carbon Lennard-Jones (LJ) potentials as described in Ref. 19. Briefly the energy is calculated using

$$V = \sum_i \sum_{i < j} [V_r(r_{ij}) - B_{ij}V_a(r_{ij}) + V_{vdw}(r_{ij})], \quad (1)$$

where V is the binding energy, r_{ij} is the distance between atoms i and j , V_r is a pair-addictive term that considers the interatomic core–core repulsive interactions, and V_a is a pair-addictive term that models the attractive interactions due to the valence electrons. In addition, B_{ij} is a many-body empirical bond-order term that modulates valence electron densities and depends on atomic coordination and the bond angles. Finally, V_{vdw} is the contribution from the LJ potential²⁰ and is only nonzero after the short-range REBO potential goes to zero.

The simulations proceed through the numerical integration of Newton's equation of motion with a time step of 0.2 fs. This many-body potential has been extensively used to study thin-film formation^{1,13–17} and has been shown to provide reasonable predictions when compared against methods

^{a)}Present address: Materials Science and Engineering Program, University of California, San Diego, La Jolla, CA 92093-0418.

^{b)}Author to whom correspondence should be addressed; present address: Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611-6400; electronic mail: sinnott@mse.ufl.edu

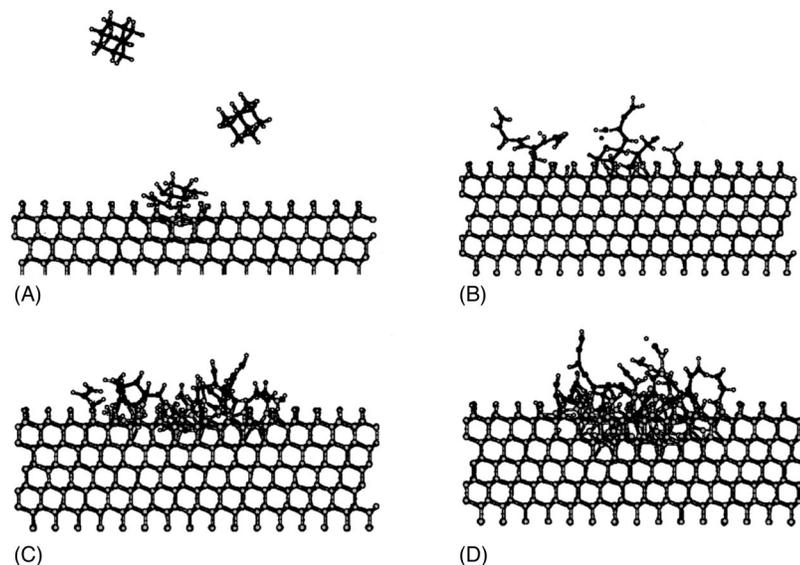


FIG. 1. Snapshots from the simulations of the adamantane molecule beam with the hydrogen-terminated diamond (111) surface. Only part of the diamond surface is shown for clarity. The black atoms represent the adamantane carbon, the gray the surface carbon, and white atoms are hydrogen. (A) A representative initial configuration of the beam at the start of the deposition at time=0.05 ps, (B) the relaxed film at time=3.0 ps after deposition at 13 km/s (119 eV/molecule), (C) the relaxed film at time=3.0 ps after deposition at 15 km/s (159 eV/molecule), (D) the relaxed film at time=3.0 ps after deposition at 17 km/s (204 eV/molecule).

derived from *ab initio* calculations.²¹ However, as is the case for all empirical potentials, there are cases where the quantitative accuracy is lacking even while the qualitative trends are correct.²¹ This potential is used despite the fact that it does not model properties that demand explicit and self-consistent inclusion of electrons, such as dipole moment and conductivity. This is because many-body, empirical potentials such as this are a reasonable way to accurately model systems containing several thousand atoms and allow for bond breaking and new bond formation during the course of the simulation in a reasonable length of time.

The adamantane beam is created from the repetition of a single adamantane molecule that has undergone equilibration at 500 K followed by quenching at 5 K. Ten of these molecules are randomly oriented in a helical pattern in the beam such that only the first and the tenth molecules impact on top of each other in the center of the substrate. The beam is roughly 15 Å in diameter and the molecules are separated from each other by about 4 Å in the direction normal to the surface. The beam starts off positioned about 4 Å above the surface. A snapshot of part of the initial configuration of the beam at the beginning of impact is given in Fig. 1(A).

The beam contains 260 atoms in the 10 impacting adamantane molecules ($C_{10}H_{16}$), and 5824 atoms in the surface. The surface is (111) hydrogen-terminated diamond and consists of 26 layers of atoms, with a $33 \text{ \AA} \times 33 \text{ \AA}$ surface area exposed to the impacting clusters. Periodic boundary conditions²⁰ are applied in the plane of the surface. The top and bottom layers are composed of hydrogen and the remaining 24 layers are carbon. The lowest 11 layers (14 carbon and 1 hydrogen) have Langevin frictional forces²⁰ applied to them to simulate the heat dissipation in a real diamond surface and to maintain the temperature of the surface at 300 K. Langevin forces are also applied to three to four rows of atoms on the edges of the surface slab. Thus, in total, 4544 of the 5824 surface atoms are Langevin atoms. The remaining surface atoms and all of the beam atoms are allowed to evolve in time with no additional constraints placed on them.

Several surface configurations were tested to determine the minimum depth of the surface that would correctly mimic the energy dissipation of a real diamond surface. The 26-layer surface prevents the artificial rebounding of impact energy from interfering with the surface reaction at the highest incident energies.

The simulations are designed to gain a better understanding of how the yield of the film increases with increasing impact velocity. Previous studies of ethylene beam deposition predict that at 13 km/s (25 eV/molecule, 200 eV/cluster), about 15% of the impacting carbon adheres to the surface, and at 18 km/s (50 eV/molecule, 400 eV/cluster) the yield is closer to 60%.¹⁷ To further explore the film formation between these velocities, simulations for the adamantane beam are conducted at velocities within a similar velocity range from 13 to 17 km/s in 1 km/s intervals (corresponding in incident energies of about 119–204 eV/molecule for adamantane), which are higher than the bond energy of adamantane of about 112 eV. For statistical purposes the results from seven simulations are averaged for each velocity. The trajectories vary slightly from one another in impact location of the beam on the substrate, where one is centered over the surface, and the other six are shifted radially from the center by about 2 Å. Each simulation runs for 3 ps, where the deposition occurs during the first 0.5 ps, and relaxation of the film occurs for the remaining 2.5 ps.

III. RESULTS

In agreement with previous studies,^{13,17} the amount of film formation with adamantane is also predicted to improve with increasing incident velocity, as shown in Fig. 2. As the molecules encounter the film, addition chemistry occurs between the molecules, or fragments of them, with the diamond surface or the nucleating film resulting in thin-film nucleation and growth. The percentage of incident molecules that adhere to the surface is about 25%–27% for impacts at 13 km/s (119 eV/molecule) and 14 km/s (138 eV/molecule).

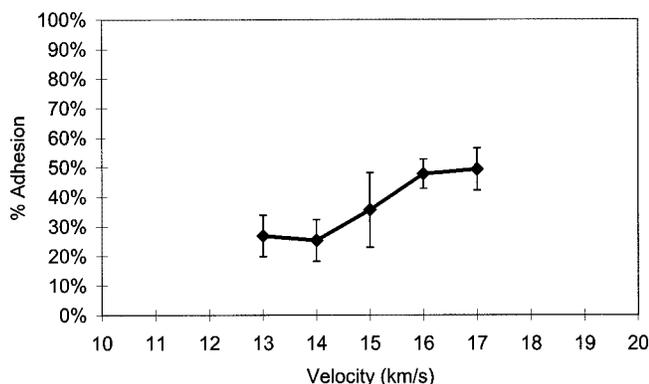


FIG. 2. Percentage of carbon atoms in the incident adamantane beam that adhere to the surface on deposition as a function of incident velocity.

This percentage increases to about 36% at 15 km/s (159 eV/molecule) and 48%–49% for impact at 16 km/s (180 eV/molecule) and 17 km/s (204 eV/molecule). Thus the simulations predict a significant transition in the velocity range of 14–16 km/s, where the percent yield of film nearly doubles in a linear fashion. The average standard deviation for the percent adhesion at the same impact velocity is about 8%.

The coordination of the carbon atoms within the film as a function of velocity is shown in Fig. 3. The highest percentage of sp^3 -type bonding exists in films formed from the impacts at the lowest velocity, in agreement with the results of other studies on similar materials.²² As the impact velocity is increased, the percentage of sp^3 -hybridized carbon atoms decreases, while the percentage of sp -bonded carbon atoms gradually increases. However, the film consists primarily of sp^2 -bonded carbon with the exact amount fluctuating between 45% and 60% over the entire velocity range.

In all the simulations some sputtering of the growing film by impacting adamantane molecules reduces the overall amount of adhesion. Consequently the thin films are largely made up of atoms from the later 8 molecules in the beam. Other fragments, particularly those that consist of more than

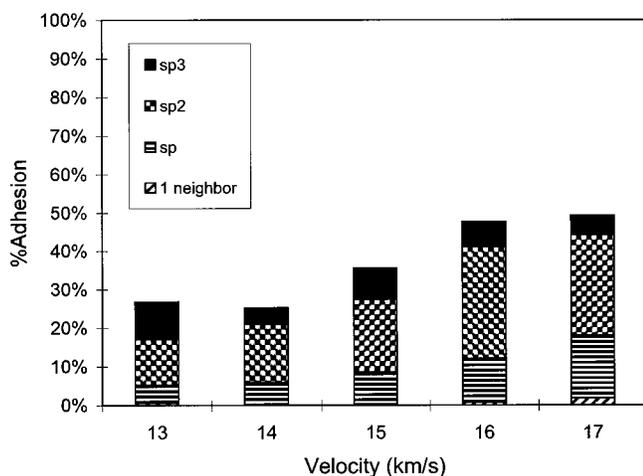


FIG. 3. Coordination of the carbon atoms in the thin films as a function of incident velocity.

8 or 9 carbon atoms, sometimes break free of the film and scatter away because of their high internal energy, as evidenced by strong vibrations and rotations. Dissociation is less likely to occur for chains that attach to the surface at more than one site. The atoms in the thin film are frequently close to atoms to which they had previously been bonded in an adamantane molecule, particularly at the lower incident velocities. At higher velocities, it is more likely for atoms from separate molecules to combine in an additive process and build on an existing film. Slight surface cratering is predicted only at the highest impact velocity considered. Most of the terminal hydrogen atoms on the diamond surface are sputtered away during deposition, although no more than 20 surface carbon atoms are removed even at the highest impact velocity.

There are other noticeable differences in the deposition outcomes over the velocity range considered in this study. At 13 km/s (119 eV/molecule), a few adamantane molecules survive the initial impact with the substrate with only a few broken bonds. These molecules impact, distort, and then scatter away from the surface. Most of these molecules, however, are further broken apart as the rest of the beam continues to deposit on the surface. Only a few of the adamantane fragments remain close to the surface and those that do join together to form mostly linear chains that are 8–10 carbon atoms in length. These chains are randomly attached to the substrate at isolated locations, as shown in Fig. 1(B). Intact molecules that scatter away are almost always at the end of the beam. The outcome of the depositions at 14 km/s (138 eV/molecule) are similar, although the adamantane molecules are broken up further which results in a small decrease of sp^3 bond character, as shown in Fig. 3.

At 15 km/s (159 eV/molecule), the initial impact causes most adamantane molecules to break apart and form linear chains. These chains are further broken apart as the beam continues to impact them. The resulting film consists of fragments roughly 3–5 carbon atoms in length that are attached to the substrate at various locations in the impact area. Very few substrate atoms are incorporated into the film at this velocity. A sample snapshot of the relaxed film formed by deposition at this velocity is illustrated in Fig. 1(C). During deposition at 16 km/s (180 eV/molecule) the cage structure of the adamantane is obliterated upon initial impact such that at most 3–5 of the original carbon–carbon bonds are left intact. As a result of addition chemistry and adamantane dissociation, linear chains of about 8–10 carbon atoms are formed that chemisorb to the substrate in various points around the impact location. Some of these chains link together while others dissociate into smaller chains as a result of the additional impacts.

At 17 km/s (204 eV/molecule) the incident molecules penetrate slightly into the surface and sometimes scatter away with substrate atoms. However, many fewer atoms from the substrate or the growing film scatter away than was the case at 15 km/s. This is due to the fact that at 15 km/s there are fewer bonds formed between the film and the substrate. The long chains that survive at velocities of 17 km/s

do so because most of them are bonded to the surface at more than one site. Figure 1(D) shows a representative relaxed film deposited at 17 km/s.

IV. DISCUSSION

The fact that the adhesion of incident adamantane molecules increases with increasing energy agrees with the results of our previous studies on molecular clusters^{13,17} and with experimental results for the deposition of polyethylene.⁴ The particular velocity range used in this study is chosen in order to compare the outcomes to our previous results obtained from the impact of ethylene molecular and cluster beams on the same diamond surface. Direct quantitative comparison of results cannot be made between the adamantane and ethylene impact simulations due to differences in the magnitude of the beams (the ethylene beam contained more than three times the number of atoms). However, the arrangements of the beams are identical and the volume occupied by each adamantane molecule, roughly 5 \AA^3 , is similar to the 8 \AA^3 volume occupied by each ethylene cluster studied previously. Hence a qualitative comparison allows for a few distinctions to be made between the outcomes of hyperthermal deposition of these two types of molecules.

The foremost difference lies in the initial reaction of the adamantane with the substrate upon impact. Due to its covalently bonded, cagelike structure, the adamantane absorbs more energy internally as its incident energy is converted into internal kinetic energy and surface kinetic energy. It distributes this energy throughout its structure before breaking apart. The ethylene clusters, held together by van der Waals bonds, dissociate on impact, allowing the individual ethylene molecules to collide with one another elastically and reactively and break apart as they bear the remainder of the impact force. Small fragments thus result from ethylene cluster beam deposition whereas the fragments from the adamantane beam deposition are larger. This difference becomes less evident as impact energy increases; the deposition of adamantane at 17 km/s yields fragments that are only 3–5 carbon atoms long, the same average length as is found for the ethylene cluster deposition. While sputtering of the film is apparent in both cases, the initial films formed from adamantane appear to survive better than the films from the ethylene clusters. This is primarily due to the larger number of sites tethering the thin film to the surface in the adamantane deposition whereas the chains formed from the molecular cluster deposition are bonded at single sites and are only reinforced if neighboring chains formed cross-linked structures.

Over the 13–17 km/s range, there is a transition point in the amount of film formation around 15 km/s, as shown in Fig. 2. It is at this velocity that the adamantane molecules began to break up their cage structure and form linear chains on impact. At this velocity, the sp^3 bonding within the film also decreases to half the amount that is present in the 13 km/s impacts, further supporting the contention that the adamantane molecules lose most of their original bonding characteristics. The sp^3 character drops to a minimal 10% at the

highest velocity. A similar trend is observed for ethylene cluster beam deposition, where at 13 km/s the film is about 35% sp^3 bonded and at 18 km/s this percentage drops to about 12%. Throughout all of the adamantane deposition simulations the dominant bonding within the film is sp^2 and the films formed from impacting adamantane molecules at this velocity are mainly polymeric in nature.

V. CONCLUSIONS

This series of simulations predict important similarities and differences for the results of hyperthermal deposition of covalently bound molecules and similarly sized molecular clusters. The similarities include increases in thin-film adhesion with incident velocity, similar sputtering and additive film formation mechanisms, and cratering of the diamond surface at high velocities. An additional similarity is that both molecular clusters of ethylene and adamantane molecules produce disordered polymeric thin films with similar structures despite their initial bonding differences. Hence depositing diamondlike molecules²³ at hyperthermal velocities is not any more likely to produce diamondlike thin films except at the very lowest incident energies.

The differences between the adamantane and molecular ethylene deposition processes include the fact that the adamantane is more likely to survive impact because of its covalently bonded cage structure whereas the van der Waals bonds holding a molecular cluster together are easily broken. In addition, when the impact forces are high enough that some of the adamantane's covalent bonds are broken, larger fragments are formed that attach to the surface at multiple locations, thus stabilizing the thin film with respect to sputtering. Thus, the adamantane molecules are, on the whole, more efficient at producing polymeric thin films at hyperthermal velocities.

ACKNOWLEDGMENTS

The authors thank Robert Whetten and Yanhong Hu for helpful discussions and gratefully acknowledge support from the National Science Foundation (CHE-9708049) and the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

¹M. B. J. Wijesundara, L. Hanley, B. Ni, and S. B. Sinnott, Proc. Natl. Acad. Sci. U.S.A. **97**, 23 (2000).

²E. T. Ada, O. Kornienko, and L. Hanley, J. Phys. Chem. B **102**, 3959 (1998).

³W. M. Lau and R. W. M. Kwok, Int. J. Mass Spectrom. Ion Processes **174**, 245 (1998).

⁴H. Usui, Thin Solid Films **365**, 22 (2000).

⁵J. C. Angus and C. C. Hayman, Science **241**, 913 (1988).

⁶K. E. Spear, J. Am. Ceram. Soc. **72**, 171 (1989).

⁷L. Diederich, E. Barborini, P. Piseri, A. Podesta, P. Milani, A. Schneuwly, and R. Gallay, Appl. Phys. Lett. **75**, 2662 (1999).

⁸V. Paillard, P. Melinon, V. Dupuis, A. Perez, J. P. Perez, G. Guiraud, J. Fornazero, and G. Panczer, Phys. Rev. B **49**, 11433 (1994).

⁹E. E. B. Campbell and I. V. Hertel, Nucl. Instrum. Methods Phys. Res. B **112**, 48 (1996).

¹⁰W. Christen and U. Even, J. Phys. Chem. A **102**, 9420 (1998).

¹¹D. Donadio, L. Colombo, P. Milani, and G. Benedek, Phys. Rev. Lett. **83**, 776 (1999).

¹²M. Kerford and R. P. Webb, Carbon **37**, 859 (1999).

- ¹³S. B. Sinnott, L. Qi, O. A. Shenderova, and D. W. Brenner, in *Molecular Dynamics of Clusters, Surfaces, Liquids, and Interfaces*, edited by W. Hase Advances in Classical Trajectory Methods, Vol. IV (JAI, Stamford, CT, 1999), Chap. 1, pp. 1–26.
- ¹⁴L. Qi and S. B. Sinnott, *J. Phys. Chem. B* **101**, 6883 (1997).
- ¹⁵L. Qi, W. L. Young, and S. B. Sinnott, *Surf. Sci.* **426**, 83 (1999).
- ¹⁶L. Qi and S. B. Sinnott, *Nucl. Instrum. Methods Phys. Res. B* **140**, 39 (1998).
- ¹⁷T. A. Plaisted, B. Ni, J. D. Zahrt, and S. B. Sinnott, *Thin Solid Films* (in press).
- ¹⁸D. W. Brenner, *Phys. Status Solidi B* **217**, 23 (2000).
- ¹⁹Z. Mao, A. Garg, and S. B. Sinnott, *Nanotechnology* **10**, 273 (1999).
- ²⁰M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1987).
- ²¹P. De Sainte Claire, K. Son, W. L. Hase, and D. W. Brenner, *J. Phys. Chem.* **100**, 1761 (1996).
- ²²M. O. Watanabe, N. Uchida, and T. Kanayama, *Phys. Rev. B* **61**, 7219 (2000).
- ²³See, for example, R. C. Fort, Jr., *Adamantane: The Chemistry of Diamond Molecules* (Marcel Dekker, New York, 1976).