

Diamond film growth by chemical vapor deposition: A molecular simulation

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We present results of a kinetic Monte Carlo simulation of low-pressure diamond film growth from a C[111] substrate via acetylene and hydrogen vapor deposition. Interactions are governed by a semiempirical interatomic potential-energy function. We find that acetylene binding to a clean C[111] surface is favored in this Monte Carlo process, but adsorption of a second C₂H₂ is not likely until the neighborhood around the site for the second-layer adsorption contains a sufficient number of first-layer adsorbed molecules. This property of the potential energy is responsible for layer-by-layer growth of the film. We also find that the simulated surface is somewhat rougher than diamond surfaces studied by atomic force microscopy. This suggests a need to include the methyl radical in future simulation models.

I. INTRODUCTION

In recent years there has been a great deal of activity directed towards the low-pressure synthesis of diamond films by a wide variety of methods including high-temperature activation, microwave-assisted plasma discharge, laser-assisted deposition, and oxyacetylene flame-assisted methods.¹⁻³ The oxyacetylene growth method is of interest because of its basic simplicity, employing a fuel-rich flame from an oxyacetylene torch and a water-cooled substrate. Growth rates of up to 150 μm/h have been reported.⁵⁻⁹ Direct observation of films by scanning microscopy^{10,11} and atomic force microscopy¹² show that the film surface is rough on an atomic scale, while on a larger scale planar structures 25-50 Å in size and with [111] orientation are visible in some cases.^{10,12} This suggests a correlation length on the order of a few tens of angstroms on the surface.

In spite of the above experimental advances, theoretical progress in elucidating some of the elementary growth mechanisms in oxyacetylene flame-induced diamond film growth has been slow. Frenklach and Spear have proposed an elementary-reaction mechanism,⁴ in which the main monomer growth species is acetylene and the reaction mechanism consists of two alternating steps: surface activation by H-atom abstraction and subsequent adsorption of an acetylene molecule. The adsorbed acetylene is attached to the diamond substrate by a single C-C bond. A subsequent hydrogen-atom transfer forms a radical site at which a second C₂H₂ can attach. Frenklach has recently carried out ballistic Monte Carlo simulations of this process assuming constant reaction rates, ignoring the hydrogen extractions and transfers, and also including methyl radical, CH₃, in the vapor phase.¹³ The results of the simulations are that the methyl radicals attach readily to the substrate, and, after hydrogen abstraction, provide additional sites for acetylene adsorption. Harris and Belton¹⁴ have suggested on the basis of thermochemical analysis that the mechanism of Fren-

klach and Spear⁴ may not lead to diamond film formation because the desorption of the second acetylene may occur at a rate which is similar to the adsorption rate.¹⁵ They propose as an alternative that acetylene binds to the substrate via the formation of *two* C-C bonds simultaneously. Recent experimental studies¹⁶ indicate that film growth rate is not correlated with acetylene concentration in the flame, but is proportional to the methyl radical concentration. Other recent thermochemical studies suggest an important role played by the methyl radical in diamond film growth.^{17,18}

Much of the current theoretical modeling work is based upon assumed reaction rates which are at best only poorly understood under the physical conditions present during diamond film growth. Efforts to better understand these conditions and their effect on reaction rates can come from molecular simulations. Harris and Goodwin have utilized molecular mechanics force fields and energy minimization programs to better understand surface thermodynamics of diamond films.¹⁷ Zhao, Carmer, and Frenklach have recently performed molecular dynamics of surface reactions of acetylene at the diamond [111] surface.¹⁹ Angus *et al.* have done a Monte Carlo simulation of film growth starting from a twinned nucleus and using constant assumed probabilities for carbon atom addition and removal.¹⁰ Because transition probabilities were assumed rather than calculated from a potential surface, a simulation of up to 2750 atoms was possible, and a twinned crystal structure was found in the simulated film.

In molecular modeling work, the choice of the potential surface is critical. Recently, Brenner developed a semiempirical potential energy function²⁰ which is designed for condensed phase hydrocarbon modeling, and which is parametrized to fit a large data base of known hydrocarbon atomization energies very closely. This provides workers who wish to carry out molecular-dynamics and Monte Carlo simulations of diamond film growth with a potential surface which is likely to be an improvement

over the generalized potential surfaces found in most molecular modeling software packages. The potential was tested by Halicioglu²¹ by comparing it with an earlier potential due to Tersoff.²² Both potentials produce comparable results. Garrison *et al.* have used this potential function in a molecular-dynamics study of dimer opening on a diamond [001] surface.²³ Peploski, Thompson, and Raff have used the Brenner potential surface in a molecular-dynamics study of reactions between C₂H₂, C₂H, and a [111] diamond substrate. Their calculations show that, while C₂H₂ adsorbs readily to a clean diamond substrate, the adsorption of a second acetylene is far less dynamically stable.²⁴ This supports the earlier conclusion of Harris and Belton.¹⁴

The purpose of the present paper is to describe results of a kinetic Monte Carlo (KMC) study of acetylene-based diamond film growth from a C[111] substrate. We have used the Brenner potential No. 2 (Ref. 20) to simulate the interaction of hydrogen and acetylene with a C[111] substrate. The simulation model allows for surface hydrogen activation and deactivation, for both the addition and desorption of acetylene, and for relaxation of adsorbed molecules.

II. METHOD

A diamond [111] substrate consisting of 200 carbon atoms was initialized with H atoms attached to the bare carbon tetrahedral bonds. Gas-phase acetylene and hydrogen were moved in a directed random walk towards the substrate. When vapor and substrate molecules approached to within cutoff distances prescribed by the Brenner potential, appropriate reactions were considered. Acetylene-substrate reactions consisted of breaking the C≡C bond to produce a C=C bond, and a new C_s-C bond along the direction of the unpaired bond of the surface carbon, C_s. During each KMC pass through the system adsorbed C_s-C molecules were also given an opportunity to desorb or to relax through random rotations about C_s-C bonds. A comprehensive computer program was developed to consider all different possible interactions between adsorbed dimers and the surface, between gas-phase and surface molecules, and between neighboring adsorbed dimers, which contribute to growth of the crystalline phase. As is true of any Monte Carlo walk in configuration space, this entails jumps over potential barriers separating low-energy configurations. Since actual rates for these jumps are not known, it is not possible to assign a rigorous time scale to a kinetic Monte Carlo simulation.

Energies before and after each KMC step were calculated from the Brenner potential, using parameter set No. 2.²⁰ This potential consists of sums of Tersoff²² type exponential potentials for C-C bonding,²² but with embedded empirical corrections for many-body interactions. The potential surface contains 70 parameters which are utilized to fit energies of atomization for simple alkanes, alkenes, alkynes, aromatics, and radicals. Potential I and potential II differ in the parameter sets, with potential II being slightly favored, in our estimation, for the diamond [111] surface. Once energy differences were determined after a move, the Kawasaki dynamical Monte Carlo criterion²⁶⁻²⁸ was applied to determine whether the event was accepted or rejected. Simulations were run on the Cray YMP at the National Center for Supercomputing Applications at the University of Illinois at Urbana-Champaign. In a second set of runs desorption was "turned off" to determine the effect on the structure of the film. The two sets of simulations consisted of 15-K and 18-K KMC passes through the system, respectively, at a temperature of 1300 K.

III. RESULTS AND DISCUSSION

The results show that chemical desorption plays an important role in the process of diamond film growth. Desorption turned out to be less likely if the neighborhood of the adsorbed C=C dimer was locally similar to a clean C[111] surface. Dynamical calculations²⁴ show the same result, i.e., desorption from a clean C[111] surface is unlikely but it is highly probable from other surface structures. In other cases (e.g., a C=C adsorbed to an isolated C_s-C) desorption occurred easily, resulting in a free C≡C molecule. Desorbed acetylene was then allowed to randomly move near the surface to attempt to readsorb at a different site. We have found that some acetylenes experience several adsorption and desorption events before becoming part of a tetrahedral (and therefore stable) structure. This desorption and surface diffusion led to a layer-by-layer growth of the film in the simulations, as each layer tended to reach at least 50% coverage before the next layer began to take shape. By comparison, when desorption was turned off the film took on a dendritic structure, with poor crystalline order in any layer. Tables I and II show the coverage of the first three grown layers with and without desorption, respectively, as a function of the number of kinetic Monte Carlo steps (KMCS). The tables show that in the former case layers have greater coverage than in the latter case, and therefore greater crystalline order. It is established that, in general growth problems, the mechanism of desorption

TABLE I. The coverage of diamond film growth for each layer with desorption.

KMCS (×1000)	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	15.0
Layer 1 (%)	0.0	21.0	37.0	55.0	66.0	70.0	75.5	76.5	80.0
Layer 2 (%)	0.0	2.0	8.0	18.0	38.0	52.0	60.0	61.5	64.0
Layer 3 (%)	0.0	0.0	2.0	2.0	2.0	4.0	20.0	34.0	38.0
Layer 4 (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.0	14.0

TABLE II. The coverage of diamond film growth for each layer without desorption.

KMCS ($\times 1000$)	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0
Layer 1 (%)	0.0	7.0	10.0	17.0	21.0	28.0	30.0	31.0	36.0	36.0
Layer 2 (%)	0.0	0.0	2.0	2.0	2.0	2.0	4.0	6.0	6.0	13.0
Layer 3 (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0

and surface diffusion is an aid in the improvement of the quality of the resulting crystal.²⁹ However, the effectiveness of this mechanism must depend in each case on the details of the interactions between adsorbed, gas-phase, and substrate atoms. Our simulations show clearly the effect of surface interactions under the Brenner potential.

Figure 1(a) shows the average height of the crystalline film as a function of the number of KMC steps, for the runs in which desorption was allowed. One can also observe in this figure three regions in the height curve where there is a reduction in slope, followed by an increase in slope. The periodic leveling off of the growth curve is due to successive filling of layers 1, 2, and 3, respectively. The curve does not become perfectly flat at these "plateaus" because the average height still increases as a layer fills, but the rate of increase is slower than during the initial formation of a new layer. Figure 1(b) shows a similar plot

for the simulation with no surface desorption. Comparison of Figs. 1(a) and 1(b) shows clearly that the crystalline film grows more rapidly when desorption occurs. When desorption is not allowed branched structures containing C=C bonds form and impede the crystallization process (the branched structures are not counted in the average height calculation). Figures 2(a) and 2(b) depict the extent of the tetrahedral crystallinity of the adsorbed film for the cases of desorption allowed, and not allowed, respectively. The ratio of tetrahedrally bonded carbon to deposited acetylene is about a factor of 2 greater for the former case than for the latter case. Figure 3 is a snapshot of the configuration of the substrate plus film after 15-K KMC passes for the model which includes desorption. Four tetrahedrally coordinated layers can be seen, with a number of adsorbed structures containing C=C

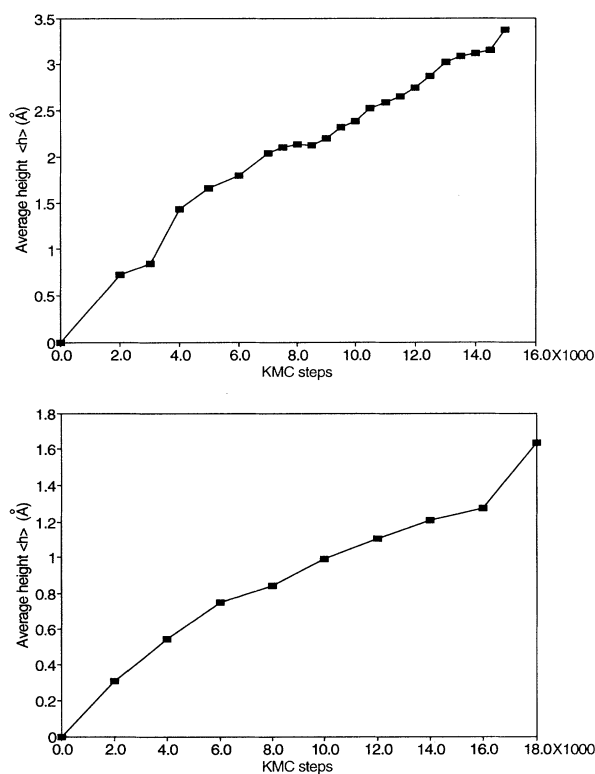


FIG. 1. (a) Plot of the average height of the crystalline film against the KMC step number for the simulations in which desorption occurred. (b) Plot of the average height of the crystalline film against the KMC step number for the simulations in which desorption did not occur.

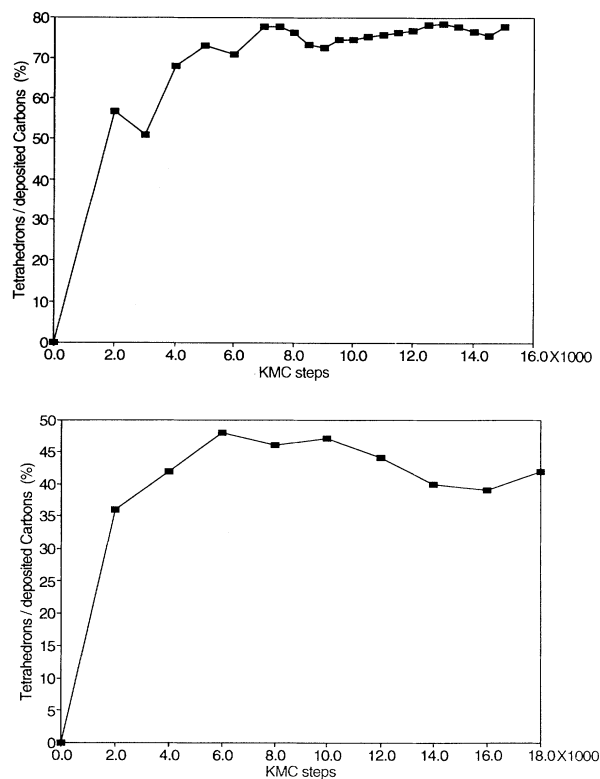


FIG. 2. (a) Plot of the ratio of tetrahedrally bonded adsorbed carbon to the total number of deposited carbon atoms for the case in which desorption occurred. (b) Plot of the ratio of tetrahedrally bonded adsorbed carbon to the total number of deposited carbon atoms for the case in which desorption did not occur.

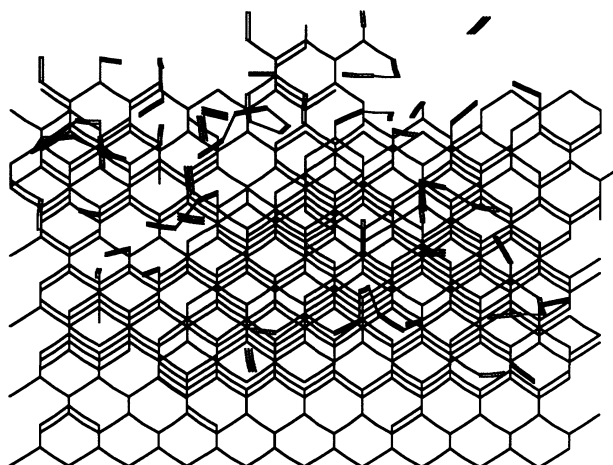


FIG. 3. Snapshot of a simulated film after 15-K KMC steps with desorption allowed. Picture shows the [111] substrate and up to four adsorbed layers, tilted slightly towards the viewer. Single lines are C-C tetrahedral bonds, short double lines are C=C bonds, and the shortest triple lines are C≡C bonds.

bonded pairs (the double lines) and vapor-phase acetylene (the triple lines).

Due to the complexity of the potential surface we used, the simulation cells are necessarily small. This makes it impossible to observe micrometer scale structures in the simulations. However, it is possible to compare our results with atomic scale measurements done by atomic force microscopy (AFM). Figure 4 is a plot of the height of the top carbon at each lattice site from the configuration in Fig. 3. Figure 4 reveals roughness on the atomic scale with a maximum amplitude of about 5 Å. By comparison, AFM micrographs show roughness on an atomic scale with maximum amplitude of about 3 Å.²⁵ This difference could be a finite size effect in the simulation. Larger simulations are currently in progress to test this. But, as discussed in the Introduction, it is plausible that acetylene dimers are not the only growth species, and perhaps not even the primary one. The dimeric nature of acetylene presents slightly greater excluded volume problems than, say, methyl radical, and this should produce slower growth and rougher surfaces. Future sim-

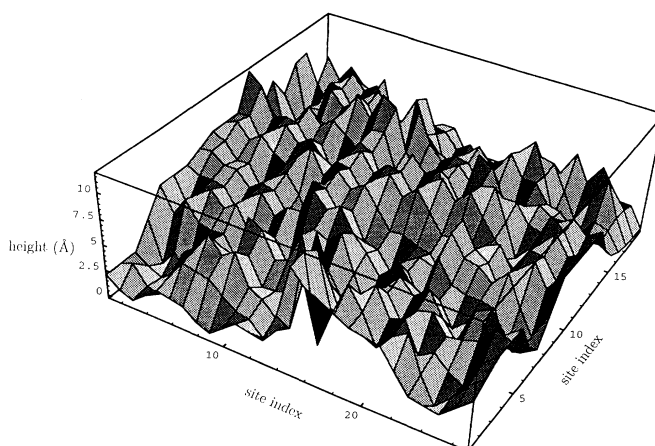


FIG. 4. Surface plot of the top carbon at each lattice site for the configuration of Fig. 3. Distance on the vertical axis is in angstroms, while the horizontal axes labels are site indices. The horizontal dimensions are 22.8×19.0 Å.

ulations will include the methyl radical in the vapor phase as a growth species.

Our simulations have demonstrated that it is now possible to model the atom-by-atom growth of diamond films by kinetic Monte Carlo methods. The potential function of Brenner²⁰ provides an excellent base for such simulations, and allows for the direct examination of the mechanisms involved in the growth process. What is currently missing is a precise time scale for the simulations. This is only available if the rates for the various reactions are known.³⁰ Ongoing molecular dynamics calculations of these rates by Raff and co-workers, as well as others, will make this information available in the near future. Future KMC simulations will also involve larger substrates, and will include other growth species, in particular the methyl radical, in the models.

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