COMBINING MOLECULAR DYNAMICS AND MONTE CARLO SIMULATIONS TO MODEL CHEMICAL VAPOR DEPOSITION: APPLICATION TO DIAMOND

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ABSTRACT

Gas-surface reactions of the type that contribute to growth during the chemical vapor deposition (CVD) of diamond films are generally completed in picoseconds, well within timescales accessible by molecular dynamics (MD) simulations. For low-pressure deposition, however, the time between collisions for a surface site can be microseconds, which makes direct modeling of CVD crystal growth impossible using standard MD methods. To effectively bridge this discrepancy in timescales, the gas-surface reactions can be modeled using MD trajectories, and then this data can be used to define probabilities in a Monte Carlo algorithm where each step represents a gas-surface collision. We illustrate this approach using the reaction of atomic hydrogen with a diamond (111) surface as an example, where we use abstraction and sticking probabilities generated using classical trajectories in a simple Monte Carlo algorithm to determine the number of open sites as a function of temperature. We also include models for the thermal desorption of hydrogen that predict that growth temperatures are not restricted by the thermal loss of chemisorbed hydrogen.

INTRODUCTION

In the chemical vapor deposition (CVD) of diamond films, an activated source of hydrocarbon molecules impinges on a substrate depositing a diamond coating. For low-pressure filament-assisted CVD, copious amounts of atomic hydrogen, produced at a hot metal filament, are combined with lesser amounts of various hydrocarbon molecules above the surface. The atomic hydrogen maintains a saturated diamond surface during growth while at the same time producing a few reactive radical sites via abstraction of chemisorbed hydrogen. The addition of carbon to the surface occurs by reactive collisions of the hydrocarbon molecules with the reactive radical sites. Under typical conditions (pressures of $\approx$0.06 atm), diamond films are produced at a rate of up to a few μm/hour.[1]

A simple analysis of low-pressure deposition reveals processes occurring on two very different timescales. First, atomistic dynamics such as those occurring during the abstraction and addition reactions are known to occur on a picosecond timescale, making these processes well-suited for modeling using classical trajectory methods. Macroscopic growth, on the other hand, occurs on a much longer timescale and so cannot be directly modeled using trajectory methods. This discrepancy in timescales can be traced to the collision rate. For example, at a partial pressure of 0.1 torr and a temperature of 1100 K, hydrogen atoms will collide with a surface at a rate of $\approx 10^{21}$ collisions/sec/cm^2, or about one collision per surface atom every 2 microseconds for a diamond (111) surface. This clear distinction between the atomistic chemical dynamics and collision rates suggests that an effective method for modeling the CVD of diamond films is to model the dynamics of the gas-surface collisions using trajectory techniques, and then use the predicted reaction mechanisms and probabilities (generated from ensembles of trajectories) as input into a Monte Carlo simulation of growth. One of the advantages of this approach over more traditional reaction-rate-based methods is that gas-surface reaction mechanisms and rates,

which remain controversial for diamond CVD, are determined from the classical trajectories and not assumed prior to the calculation.

The primary goal of this paper is to illustrate this combination of molecular dynamics and Monte Carlo methods using the reaction of atomic hydrogen with a diamond (111) surface as an example. We do this by first calculating abstraction and sticking probabilities at various temperatures using an ensemble of trajectories of atomic hydrogen reacting with both a fully saturated (111) surface and one containing a single radical site. We then use this data in a Monte Carlo algorithm to estimate the average number of open sites on a (111) terrace under typical low-pressure CVD conditions.

The secondary goal of this work is to explore the role of thermal desorption in limiting substrate temperatures for which good diamond growth occurs. Hydrogen desorbs under ultra high vacuum from the (111) surface beginning at $\approx$1100 K.[2] It has therefore been suggested that thermal desorption may be limiting growth temperatures since low-pressure growth of high quality diamond films has been confined to substrate temperatures below $\approx$1370 K.[2,3] However, growth using an oxyacetylene torch appears to contradict this since diamond films have been deposited at temperatures as high as 1770 K.[4] To reconcile these results, it has been suggested that the higher flux of atomic hydrogen in the oxyacetylene torch is sufficient to keep the surface hydrogen terminated at the higher temperatures.[4] To further explore this issue we have included models for thermal desorption in these calculations. Contrary to previous suggestions, our models predict that hydrogen coverage on the (111) surface is independent of the flux of atomic hydrogen at substrate temperatures much higher than those for which high-quality growth is no longer achieved in low-pressure CVD, suggesting that thermal desorption of hydrogen is not responsible for limiting growth temperatures under these conditions.

CLASSICAL TRAJECTORY CALCULATIONS

To model a (111) surface, we use an infinite slab of 12 layers of carbon atoms with each layer containing four atoms. Periodic boundaries are used in the two directions parallel to the surface leaving two infinite (111) surfaces top and bottom. The substrate temperature is maintained by applying a thermostat to the middle four layers.[5] The calculation is first initiated by equilibrating the substrate to the chosen temperature. Batches of a total of 400 hydrogen atom trajectories, separated by 10,000 equilibration steps, are then run by colliding single H atoms with both the top and bottom surfaces. For a fully hydrogen terminated surface three batches were run at each temperature, while four batches were run for surfaces containing a three-quarter coverage of hydrogen (i.e. one radical site per surface). We also ran a single batch of trajectories on a substrate that had layers containing 16 atoms and four equally spaced radical sites at 1200 K. Sticking and abstraction probabilities calculated with this larger substrate are close to those calculated with the smaller substrate suggesting that our system is sufficiently large to model these processes.

Each trajectory is started by randomly choosing the coordinates in the plane of the surface of the incoming hydrogen atom and then backing the atom away from the surface until it is out of the interaction range of any of the surface atoms. The components of the velocity for each incoming atom are chosen from a Boltzmann distribution (with the sign in the direction perpendicular to the surface chosen so that the atom is initially headed toward the surface) for the same temperature as the substrate. Equations of motion are then integrated using a Nordsieck predictor-corrector[6] and a timestep of 0.25 fs until either the incoming atoms stick to the surface (defined as the incoming atom bouncing against the surface four times), or are headed away from the surface and outside the range

of interaction for all atoms still attached to the substrate. Abstraction probabilities are defined as the number of trajectories that lead to the formation of H_2 via the removal of chemisorbed hydrogen divided by the surface coverage and are averaged for both the full coverage and three-quarter coverage surfaces. Sticking probabilities are defined as the number of trajectories that lead to sticking of the hydrogen atoms to the surface divided by the number of open sites on the surface. No reactions other than sticking and abstraction were observed during the molecular dynamics simulations.

The interaction potential used is very similar to potential I of reference 7 except that the parameter S_{CH} was changed to 1.92 so that the classical barrier height for abstraction of the tertiary hydrogen from isobutane matches the experimental activation energy of 0.32 eV.[8] Previous *ab initio* cluster calculations have shown that this value should be a good approximation for the activation energy for the abstraction of hydrogen from the (111) surface.[9] Furthermore, comparison of the *ab initio* calculations with the empirical potential has shown that the empirical potential provides a realistic description of relaxation around a radical site on the (111) surface.[9]

Shown in Fig. 1 are the abstraction and sticking probabilities at three temperatures generated by the classical trajectories. Also shown is an Arrhenius function of the form

$$P = Ae^{-Ea/kT} \tag{1}$$

fit to the abstraction probabilities. The activation energy of 0.34 eV obtained from the Arrhenius fit is close to the activation energy for abstraction of the tertiary hydrogen in isobutane used to fit the empirical function, suggesting that simple Arrhenius behavior as given by Eq.(1) is an adequate description of this system where the surface and gas temperatures are equal.

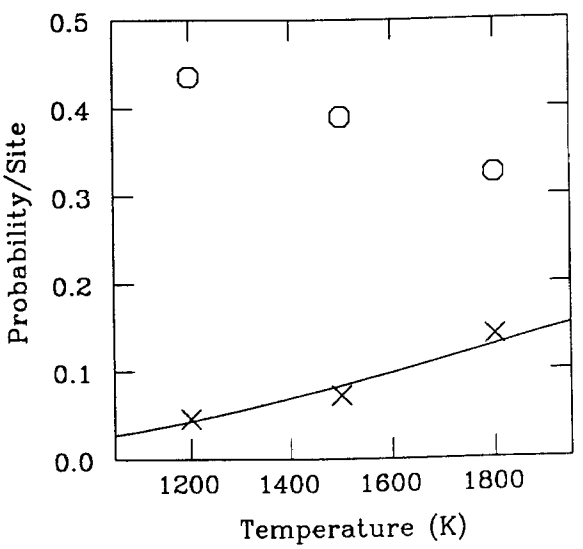

Figure 1. Abstraction (crosses) and sticking (circles) probabilities at various temperatures as determined from classical trajectories. The solid line is a least-squares fit of Eq.(1) to the abstraction probabilities (A= 1.162, Ea=0.341 eV).

MONTE CARLO CALCULATIONS

To initiate the Monte Carlo calculations, an array is defined where each element represents a surface carbon atom on a (111) terrace and the value of each element specifies whether the site is currently occupied by chemisorbed hydrogen or open for bonding. Each step in the Monte Carlo algorithm represents a colliding gas-phase hydrogen atom. If thermal desorption is excluded, each step consists of randomly choosing a surface atom (representing the site where the incoming hydrogen atom strikes) and checking whether it is already bonded to a hydrogen atom. If a hydrogen atom is currently chemisorbed to the site, then the probability for abstraction is compared to a random number. If the random number is smaller than the abstraction probability the site is changed from being occupied to being unoccupied. Likewise if the initial site is not occupied then a decision is made as to whether to occupy the site by comparing the probability for sticking to a random number. The average number of open sites can then be obtained by averaging over many steps, as can quantities such as fluctuations in the number of open sites and probabilities for various combinations of neighboring open sites. At this level the results of this algorithm do not depend on the timestep and are therefore valid for any flux. This same algorithm, using various ratios of sticking to abstraction probabilities, has recently been discussed in detail by Frenklach.[10] Our results for the average number of open sites (shown as the crosses in Fig. 2) for various temperatures are in agreement with those reported by Frenklach.

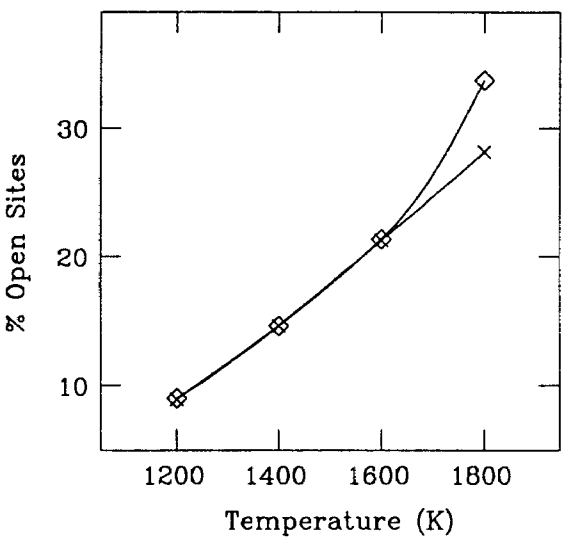

Figure 2. Number of open sites on a (111) terrace at various temperatures. Crosses do not include thermal desorption. Diamonds are for an atomic hydrogen flux at 0.1 torr and include thermal desorption.

Including thermal desorption modifies the Monte Carlo algorithm and introduces an explicit timescale because the probability for thermal desorption is time dependent. Because each step is considered one collision with the surface, the time is updated at each step in increments of the reciprocal of the flux of atomic hydrogen. At the beginning of each timestep the loss of hydrogen is evaluated by assigning individual probabilities for thermal desorption. This probability is calculated from the expected number which will thermally desorb within this timestep based on the rate law equation and the current surface concentration. The total number of atoms to desorb is then calculated by using the probability for N independent occurrences based on the binomial distribution (BD) [11]

and obtaining the maximum number to desorb for which the BD probability for occurrence is less than a random number. This number of atoms is then randomly removed from filled surface sites, the collision occurs and the algorithm as outlined above is repeated.

Two models for thermal desorption are used in these calculations. First, following the recent experiments of Schulberg *et al.*,[12] we assume first-order kinetics with a rate of the form of Eq.(1) with parameters A=5x10^7 sec^{-1} and Ea=2.21 eV. Fig. 3 shows a simulated thermal programmed desorption (TPD) peak and the number of open sites derived from the Monte Carlo algorithm assuming a perfect vacuum and a heating rate of one degree kelvin per second. The calculation shows a relatively sharp desorption peak centered at 1180 K in agreement with experiments on the (111) surface.[12,13] Substitution of this model into the Monte Carlo algorithm and using an atomic hydrogen flux assuming a partial pressure of 0.10 torr yields a neglible change in the number of open sites on the (111) surface. Apparently the sticking of hydrogen to the surface at this flux, which is appropriate for low-pressure CVD, is sufficient to account for any loss due to thermal desorption.

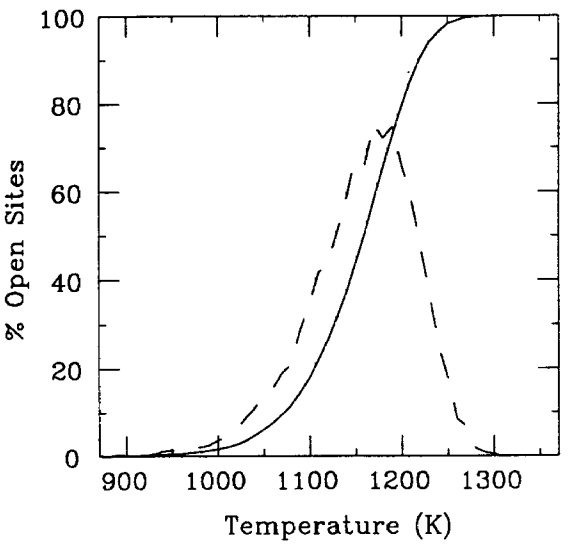

Figure 3. Simulated TPD peak (dashed line, arbitrary units) and number of open sites (solid line, units at left) generated from the Monte Carlo algorithm.

For the second model we again assume first-order desorption and a rate given by Eq.(1). For this case a prefactor of 8.8x10^{13} sec^{-1} is used which is derived from the vibrational frequency for the empirical potential for a hydrogen atom on a diamond (111) surface. We assume that desorption of atomic hydrogen occurs from the lowest vibrational states for chemisorbed hydrogen, so we take as the activation energy the carbon-hydrogen bond strength (4.134 eV from the empirical potential) minus the sum of the energies of the first three vibrational states weighted by the appropriate Boltzmann factors. Shown as the diamonds in Fig. 2 is the average number of open sites on a (111) surface including this model of thermal desorption. As can be seen, thermal desorption does not change the number of open sites except at the highest temperatures. Both models then predict that thermal desorption does not limit the temperature regime for which good diamond growth may occur on a (111) surface in the low-pressure CVD of diamond films.

SUMMARY

While the chemical dynamics associated with the reactive collision of gas-phase species with a diamond surface during the low-pressure growth of diamond films can be simulated using trajectory methods, the low collision rate makes direct modeling of CVD growth impossible. Here we have demonstrated a combination of classical trajectories and a simple Monte Carlo algorithm that can bridge this gap between short timescale chemical dynamics and longer timescale deposition. Although the example used of atomic hydrogen as the gas-phase species is relatively straightforward, the reaction of other species such as methyl radical and acetylene can also be simulated since the empirical potential used in the trajectory calculations can model these reactions. We plan to extend this approach to other gas-surface reactions as an alternative to more traditional reaction-rate-based approaches.

We have also included thermal desorption of chemisorbed hydrogen to explore whether this limits the temperature for which good diamond films can be grown. Contrary to several suggestions in the literature,[2,3,4] our model predicts that the addition of atomic hydrogen to a diamond (111) surface under typical low-pressure CVD conditions can compensate for the thermal loss of hydrogen even at temperatures at which high-quality diamond films are no longer deposited.

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