

MOLECULAR MODELING OF CVD OF (111)-ORIENTED DIAMOND FILM USING A KINETIC MONTE CARLO METHOD

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Introduction

The CVD of diamond from a small amount methane in hydrogen at subambient pressures has become commercially viable during the last decade.[1] The gas mixture is heated by hot filaments or plasmas to dissociate the hydrogen, and the H atoms bond to the surface carbon atoms to passivate it by forming sp^3 bonds.[2] While it is well understood that deposition of diamond involves incorporation of chemisorbed hydrocarbon radicals, the details of the diamond growth mechanism are still not well understood. There are several different modeling approaches used to analyse the diamond growth process. Molecular dynamics simulations are used to model depositions, but only over milliseconds.[3] Recently, Dawnkaski et al. and Battaile et al. performed 3D atomic scale simulations of the (100) and (111) diamond surface growth. [4,5]The original model of Battaile has been developed in the present work to include the fact that the same chemical reaction will be different depending on whether the reaction occurs on step edges or surface terraces. The method allows the surface chemistry, local atomic coordination, and surface structure to be incorporated into the simulation, and is capable of simulating hours of deposition under commonly used deposition conditions.

Procedure

The growth of diamond film by CVD is simulated by using a rigid diamond type lattice. Initially, six (111) planes of the diamond lattice are filled with carbon atoms to form a substrate six layers thick. To passivate the top layer, the substrate is terminated with a layer of atomic H. Figure 1.

The growth of diamond requires either desorption or abstraction of the chemisorbed atomic H. The active site that is formed may either chemisorb back an H atom, or a hydrocarbon molecule or radical. Similarly, the hydrocarbon may desorb, or react by one of the possible surface reactions that leads to carbon atom incorporation into the diamond lattice.

The surface reaction rate constants are those reported by Battaile. The kinetics of surface reactions are represented by the general formalism used in the Surface ChemKin computer program.[6] A schematic of the atomic arrangements for one of the surface reactions included is

presented in Figure 2. The dashed line indicates the film surface. Forward and reverse rate constants were calculated, as well as the reaction rates at surface steps and terraces.

The temporal evolution of the diamond film during growth is simulated using the Monte Carlo method developed by Battaile et al. One surface reaction is allowed to take place at one surface site during each time step. The occurrence of one of the reactions at one of the sites is termed an event. At each time step, a list of all possible events is constructed, and the probability for each event is proportional to the associated surface reaction rate, relative to the rates for all other possible events. Then, a random number is generated to select the event, and the process is repeated. The method uses a variable time step to account for the fact that different events take place at different rates.

Results

The atomic structure of the (111) diamond surface at three different stages of deposition under the CVD conditions typical for a hot filament reactor- feed gas 0.9% CH_4 , 7% Ar, and 92.1% H_2 , and gas temperature equal to 1720K with a substrate temperature equal to 1500K- are shown in Figure 3. The atomic surface structure is dominated by islands of new (111) layers at short times (Fig 3a). As deposition proceeds, lateral growth of the islands occurs, which occasionally leads to coalescence (Fig 3b). At long times, the surface structure reaches a dynamic equilibrium, in which existing incomplete (111) layers are being filled in by carbon adatoms, while new (111) layers are also being formed (Fig 3c).

The effect of process parameters on the atomic surface structure was studied under a standard set of conditions- 0.4% CH_4 , 7%Ar, 92.6% H_2 , $T_g=1720K$, $T_s=1500K$, and $P=20.25$ torr (Case I)- using the SPIN Computer program originally developed by Dandy and Coltrin.[7]. The effect of decreasing the substrate temperature to 1073K, and increasing the methane pressure to 7% were also studied. In the case of the high methane partial pressure, and high substrate temperature, 1.8% H atoms were found embedded in the diamond film. Careful analysis also showed 0.2% embedded H atoms in the lower substrate

temperature film as well. No embedded H atoms were observed at the lower partial pressure of methane. The average concentration of vacancies was found to be as follows: High substrate temperature: 0.8% and 1.4% for 0.4% and 7% methane respectively, and for low substrate temperature: 0.1% and 0.3%. This result shows that substrate temperature has the largest effect on vacancies.

Surface roughness calculations also show that lower substrate temperature and lower methane partial pressure lead to smoother deposits.

Summary

A kinetic Monte Carlo program with a variable time increment was employed to study the CVD of (111) diamond surfaces at two substrate temperatures and two methane concentrations. The deposition rates are in general agreement with hot filament reactors. The quality of the film decreases with increasing deposition rate. Therefore, for a given application with its specified level of defects, one can determine a suitable substrate temperature, and feed gas chemistry which results in the maximum deposition rate.

Acknowledgements

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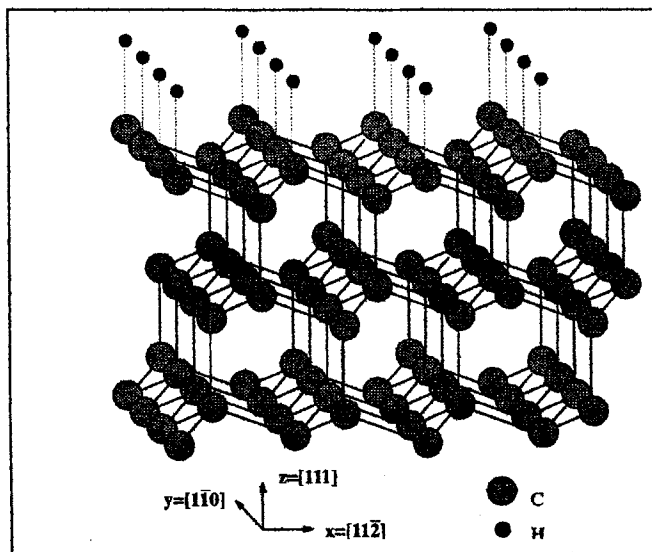


Figure 1 Section of Diamond Substrate. Diamond atoms are open circles; hydrogen filled.

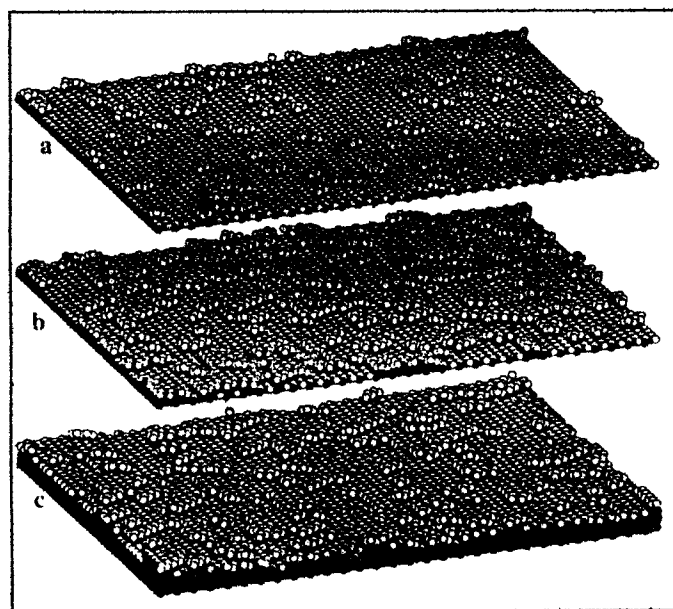


Figure 3 Typical Diamond Surface Structure

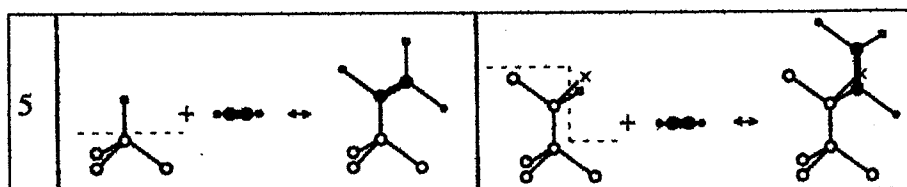


Figure 2 A Surface Reaction for Acetylene Addition. Left is terrace; right is step. Dotted line is film surface.