TITLE BARRIER TO THE NUCLEATION OF METHYL GROUPS
ON THE DIAMOND (111) SURFACE

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ABSTRACT

Questions about the mechanism of diamond film growth by low-pressure, plasma-assisted chemical vapor deposition methods have persisted for some time now. As an attempt to explore one aspect of the problem, we examine the energetics of several adsorbed diamond (111) surfaces. The adsorbates are mixtures of methyl groups and hydrogen atoms. The model for these systems is the molecular orbital hamiltonian of Dewar and coworkers.

From these calculations we find that H adsorbtion is preferred due both to bond energy and steric effects. Thus nucleation of a cluster of three or more methyl groups, as assumed in earlier work, is energetically very demanding.

INTRODUCTION

Recent interest in the growth of diamond thin films has stimulated the study of single crystal diamond surfaces in ever greater detail [1]. The hope is that such studies will eventually contribute to a synthetic path way for the epitaxial growth of high quality, crystal films on a variety of substrates. One sythetic approach, diamond growth by plasma-assisted chemical vapor deposition, possesses a bewildering number of variables. Understanding the detailed morphology and behavior of diamond surfaces may shed light on the roles played by some of these variables. In general, we want to know what the chemistry of the deposition in the near-surface region (Fig. 1) so that we will know what we want the plasma to do. It must be added, however, that the degree
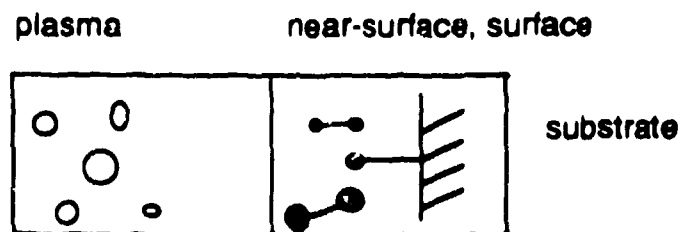

Figure 1. Schematic of CVD reactor. The areas of concern here are the near-surface and surface regions.

to which the state of the diamond surface is controlling the growth process is still a topic of intense debate.

The premise of this work is that the surface is of substantial importance and we proceed on that basis. One of the major theories of diamond film growth is that the termination of the surface changes the carbon-carbon particle spacings which, in turn, promotes or inhibits the growth of diamond over graphite due to lattice matching constraints. In particular, both experimental and theoretical work shows that the atomic level behavior of diamond surfaces is sensitive to both temperature and chemical environment. Below 1200 K, the (111) surface, for instance, is in a 1X1 configuration as observed by LEED. Above that temperature, the surface reconstructs to a 2X2 or a 2X1 pattern. There are several theories about the detailed nature of the reconstruction. The one which seems most favorable in terms of its ability to account for the most experimental data is the 2X1 pi-bonded reconstruction of Pandey [2,3]. These are motivated by analogy to Si surfaces. On the other hand, addition of any of several adsorbates restores the diamond (111) surface nearly to its bulk configuration.

Here we report numerical results on various surfaces and modified surfaces of diamond (111), based on a molecular orbital model of the surfaces [4]. These are the relative energies of various mixtures of H and methyl group termination of the surface, clean surface reconstruction as described within the model, and estimates of the energy required to remove a methyl group or a hydrogen atom from the surface as a function of coverage. We have chosen H and methyl group coverage in order to compare with earlier work [5]. There it is assumed that some sort of methyl group coverage arises spontaneously. Then it is argued that it is possible to promote some sort of epitaxy by gas-phase attack of a cation.

However, the present calculations give a picture of the difficult incurred by trying to initiate nucleation of a cluster of methyl groups on the (111) surface. The reason for this is that the H terminated surface is so much more favorable energetically. The difference arises from both bond energy and steric interferences. A compounding factor is the frequency with which clusters of methy groups form so that some initiation of growth can take place. The question of the frequency and barriers associated with nucleation naturally lead to concerns about the details of the deposition mechanism. These might fall into two categories, one being Eley-Rideal (ER) like and the other being Langmuir-Hinschelwood (LH) like [6]. At some future date, it may be profitable to identify which mechanism dominates under which plasmatic conditions .

The conclusion of the present study is that the presence of H is a two-edged sword. On the one hand, it does stabilize the (111) surface to maintain the diamond lattice in the presence of the plasma. On the other, it may imposes a serious barrier to the attachment of methyl groups to the surface, thereby inhibiting growth. Naturally, as the experimental evidence for what the dominate reactive species in various plasmas becomes more apparent, it will be desirable to study the relative adsorbation of those species as well.

The remainder of the paper is as follows. The next section describes the numerical and strategic methodology used. The section after that presents the results of the computations. The final section summarizes the salient points of the research and points out a few of the poosible directions of future work.

METHOD

Numerical

Our numerical method is based on a semiempirical molecular orbital theory of organic molecules and polymers due to Dewar, Thiel, Stewart and others [4]. An orbital matrix equation whose matrix elements are approximated using experimental data is produced from the theory. The particular approximations used here is referred to as the AM1 hamiltonian. The form of the individual matrix elements is based on the Hatree-Fock equations for the system. The approximations serve two purposes : 1) The calculation of matrix elements is greatly reduced and 2) The use of experimental data allows inclusion of some important correlation effects neglected in the formal theory.

Solving the matrix equation allows estimates of an optimum geometry, heat of formation, dipole moments, charge distributions and a variety of other properties for any given combination of atoms. The AM1 approach has been found to give reasonable properties for many molecules and ploymers, predicts a reasonable value for the lattice constant of bulk diamond and can be confidently operated with periodic boundary conditions in one dimension.

Here we focus primarily on the geometry and heat of formation of a several of related systems to be described below. A comparison of the relative stability of various adsorbates on the (111) surface of dimaond, as well as a understanding of what is driving the stability. To achieve some description of the surface, it is necessary to adopt a representation of the real physical system. In the MOPAC routine, this is done by taking the bulk cell and terminating the supposedly unexposed surfaces with hydrogen atoms and by keeping some of the carbon atoms fixed in space. Because the routines can only reliably handle periodicity in one dimension, all surfaces are, therefore, represented as strips or "polymers". In instances where two dimensional periodicity is reliable, the two representations give comparable results.

Systems

Eight different systems are considered here, namely, bulk diamond, the clean (111) surface, an H terminated surface, a surface terminated by 50% H and 50% methyl groups,a surface terminated by 25% H and 75% methyl groups, a methyl group terminated surface, a surface in which a H atom as been abstracted, and, finally, a surface in which a methyl group has been abstracted.

These choices are motivated by the following two questions. One, what is the nature of the surface reconstruction relative to bulk diamond? Two, how stable are these surfaces relative to each other? By allowing each system to find an optimum geometry, both of these questions may be answered by simple comparison. There is also a third question, namely, what is the surface coverage of H and methyl gruups as a function of temperature? This method, as it stands, can only address the last question at 0 K, but this is still of some utility. The method can be readily adapted to nonzero temperatures using suitable Monte Carlo averaging techniques.

Due to problems in calculating correlation effects, it is difficult to obtain a reliable potential energy surface at all points in configuration space. Consequently, we focus chiefly on certain key metastable configurations corresponding to relaxed or reconstructed surfaces or an abstracted system in which a hydrogen atom or methyl group has been moved to infinity. In the latter instances, the calculation assumes a biradical configuration. Otherwise, a closed-shell, restricted electronic configuration is assumed.

RESULTS

Geometries

The clean surface reconstructs in a manner similar to the pi-bonded reconstruction model of Pandey [2], but not precisely the same. The top layer of carbon atoms (Fig. 2) contracts, while the second layer dilates perpendicular to the surface. However, little dimerization is seen.
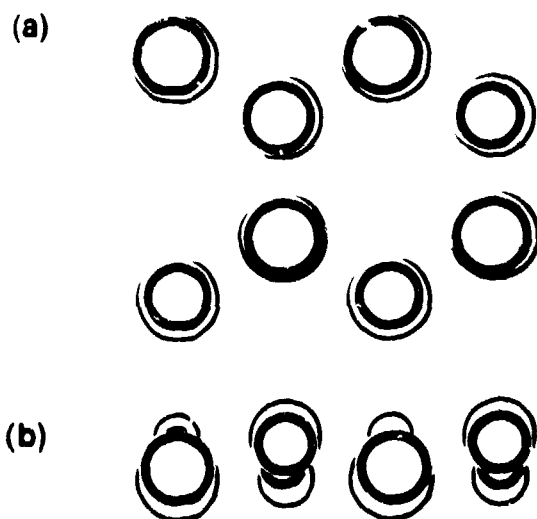
Figure 2. Clean diamond (111) surface : (a) Top view of first two carbon layers. The heavy circles represent the relaxed surface while the light circles represent the equivalent bulk atoms. (b) Side view analogous to (a). The layer spacing has decreased from 0.56 to 0.28 Å.

For all the fully terminated surfaces, near-bulk like configurations are seen for the first layer of carbon atoms which are not considered adsorbates (Fig. 3). The C-H
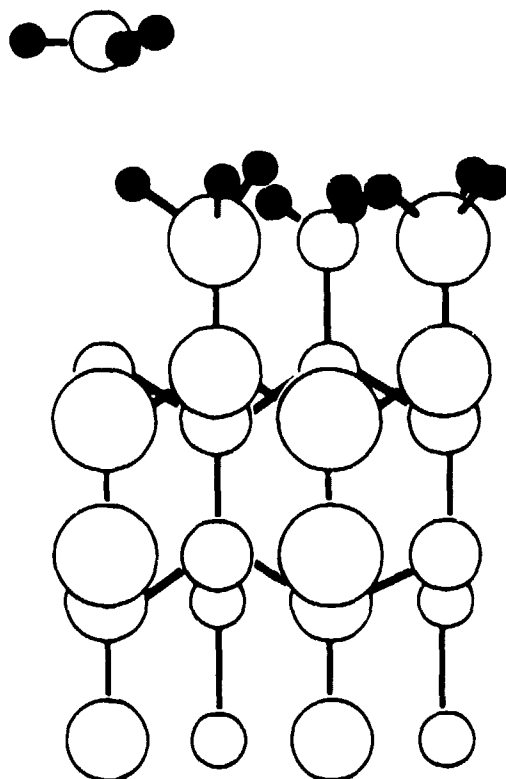
Figure 3. Methyl radical abstracted from diamond (111) surface which is covered with other methyl groups. Because of the periodicity of the calculation, the abstraction reduces the coverage to 75%. The hollow circles represent carbons, while the solid circles represent hydrogens. This figure typifies the configurations of the other seven systems reported in the text.

bond distances for the H-terminated sites are 1% longer than those in methane, while the C-H distances on adsorbed methyl groups are 1% shorter. More importantly, the H-H distances for H atoms on adjacent methyl groups can be closer than 2.4 Å, twice the van der Waals radius of an H atom. Consequently, to help alleviate some the steric interference, the CCH bond angle for the methyl groups changes as a function of coverage from nearly normal, 109°, to very oblique, 123°. One might think that the C(surface)-C(methyl) distances show some alternating pattern, but none has been found. They are all about 1.51 Å.

Binding energies

The binding energy of H atoms to the diamond (111) surface at high coverages, above 75%, is calculated to be 120 kcal/mole, compared to 102 kcal/mole found experimentally. This is considered to be an indication of the quality of the AM1 hamiltonian in describing diamond-related systems.

The binding energy of methyl groups when abstracted as methyl radicals at high coverages, above 75%, is about 105 kcal/mole. The author is unaware of any experimental data of this type at this time.

Relative surface energies

The binding energy of methyl groups when substituted for an H atom on the same surface varies from about 25 kcal/mole at low coverages, below 25% methyl-75% H, up to 130 kcal/mole at high coverages, above 75% methyl-25% H. Thus it is apparent that the H covered surface is much preferrable energetically than any amount of methyl coverage. Any appearance of methyl groups on the diamond (111) surface ought to be purely transitory. Futhermore, the energy required to cluster three methyl groups into nearest neighbor proximity is 210 kcal/mole. This energy difference is almost an order of magnitude larger tnan the one found in an earlier study of the epitaxy mechanism [5]. Note also that these are energy differences rather than actual barriers, which are generally considered to be unreliable in this method and may be substantially more than this. Also, the shape of the barrier will depend on the mechanism of deposition, i.e. ER vs. LH. In all this seems to cast some doubt about any possible role that methyl groups would play in diamond epitaxy.

SUMMARY

As found experimentally, the present molecular orbital calculations on the behavior of H covered diamond (111) surfaces show that the adsorbate restores the clean surface to a nearly bulk configuration. Coverage by methyl groups shows similar restorative powers. However, the relative energy of the H terminated diamond (111) surface is always found to be less than that of mixtures of methyl groups and H atoms. Consequently, displacement of H atoms by methyl groups seems to represent a transient phenomenon. The energy required to being three methyl groups to nearest neighbor proximity is about 210 kcal/mole. A substantial amount of this is due to steric interactions among the methyl groups. This presents an additional barrier to nucleation of methyl groups on the surface which is thought by some to be a precursor to the advent of diamond epitaxial growth.

For future work, the present research suggests the study of different adsorbed species once the relevant ones are identified through diagnostic studies, the transitory surface damage done by the plasma, the calculation and measurement of surface diffusion barriers for various surface species, and the investigation of nonhydrogenic systems.

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