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Surface migration during diamond growth studied by molecular orbital calculations

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Migration of various important species (H, CH_3, CH_2, C_2H, and C_2H_2) on a diamond (111) surface has been investigated theoretically, using a cluster approach and the second-order Møller-Plesset perturbation theory. The order of the energies (barriers) obtained for a single jump between two neighboring radical sites is $CH_2 < H < C_2H \approx CH_3$ (52, 248, 350, and 353 kJ/mol, respectively). The C_2H_2 species is assumed to migrate by an alternating onefold and difold site adsorption to the surface. The corresponding barrier obtained for C_2H_2 is 186 kJ/mol, which is somewhere in between that of CH_2 and H. The present type of surface migration of chemisorbed species will, with one exception, be energetically favorable in comparison to any desorption process. In the case of C_2H_2, a desorption process will be energetically favorable. [S0163-1829(99)00812-7]

I. INTRODUCTION

Vapor growth of diamond is a dynamic process with a large degree of complexity. It involves the generation of surface vacancies, adsorption of atomic hydrogen, and addition of growth species to various radical surface sites. Growth of diamond has usually been discussed without including explicitly the possibility for surface diffusion. However, experiments have indicated that also surface diffusion can take place during diamond growth.[1–3] Hence, the complex dynamic processes occurring during chemical vapor deposition of diamond is also assumed to include surface processes like migration of hydrogen and a different type of growth species.

It is very important to obtain a deeper knowledge at the molecular level of the surface processes during diamond growth. One important factor is the energetics during the growth. Adsorption energies, as well as barrier energies for migration, are then especially interesting to study. Migration of H and different growth species on diamond surfaces have earlier been calculated, using a cluster approach and different quantum-mechanical methods.[4–14] The activation energy for migration of the dangling bond, as well as of the C, H, and CH_2 species, on a C(001):H surface with (2×1) reconstruction have been calculated.[4–6] No migration of CH_2 was found to be possible without dangling bond assistance.[4] With the assistance of a dangling bond the E_a of the limiting step was found to be above 386 kJ/mol. Furthermore, a single C adatom was found to migrate preferably along the dimer row.[5] An adatom migration process passing through the S_A step was studied in detail in the case of C atom migration on diamond (001) surfaces.[6] It was concluded that this specific migration process easily occurs from the upper terrace to the lower one, but hardly takes place from the lower terrace to the upper one.

Recent theoretical results have indicated that bridging groups H, as well as radical vacancy, can migrate on diamond (100) surfaces.[7–10] A mechanism based on surface diffusion of chemisorbed CH_2 and $C{=}CH_2$ species, respectively, indicate that a dimer row pattern formation will serve as an attractor for migrating species.[7,8] The highly anisotropic migration of radical vacancies was found to reach 1–2 orders of magnitude larger migrations distances than those of lone CH_2 and $C{=}CH_2$ species.[8] Furthermore, H migrations between bridging groups and dimers and between surface sites and adspecies were found to be fast, comparable in rate to H additions and abstractions.[8] CH_3 and CH_2 barriers for migration along the [110] direction, in the presence of H vacancies on the monohydrogenated surface, were calculated to be high for CH_3 (261 kJ/mol) but low enough for CH_2 (194 kJ/mol) that surface migration might occur under low-pressure diamond growth conditions.[9]

Surface migration of H on diamond (110) and (111) has also been investigated by different quantum-mechanical methods.[11–13] The obtained energy barrier for H on the diamond (110) surface was 318[11] and 309[12] kJ/mol, respectively, for a single jump between neighboring sites in the {001} direction over the ridges. The lowest obtained energy barrier for a migration of H on the diamond (111) surface is between two adjacent carbon radical sites (317 kJ/mol).[13]

An important aspect to study is whether surface migration should be taken into account, or not, as a limiting step in the chemical vapor deposition of diamond (111). The purpose with the present study is, hence, to energetically investigate the migration process of different important chemical vapor deposition (CVD) species on a diamond (111) surface. Energy barriers for the different species, and for a specific jump process, will then be related to the corresponding energy of desorption (assumed to be the inverse of adsorption) for that specific species from the surface.

II. METHODS

The adsorption of gaseous species to a monoradical surface site on a diamond (111) surface has earlier been investigated by the present authors.[15] A medium-sized template $C_{13}H_{21}$ was then found to be sufficient in the adsorption studies. The framework of the template $C_{19}H_{28}$ in the present study is different (and larger) in that the two neighboring radical surface sites have identical environments; five adjacent H atoms, and one adjacent dangling bond (Fig. 1). The dangling bonds are assumed to be created by abstraction reactions including species in the gas phase. These types of surface vacancies are assumed to exist under low-pressure

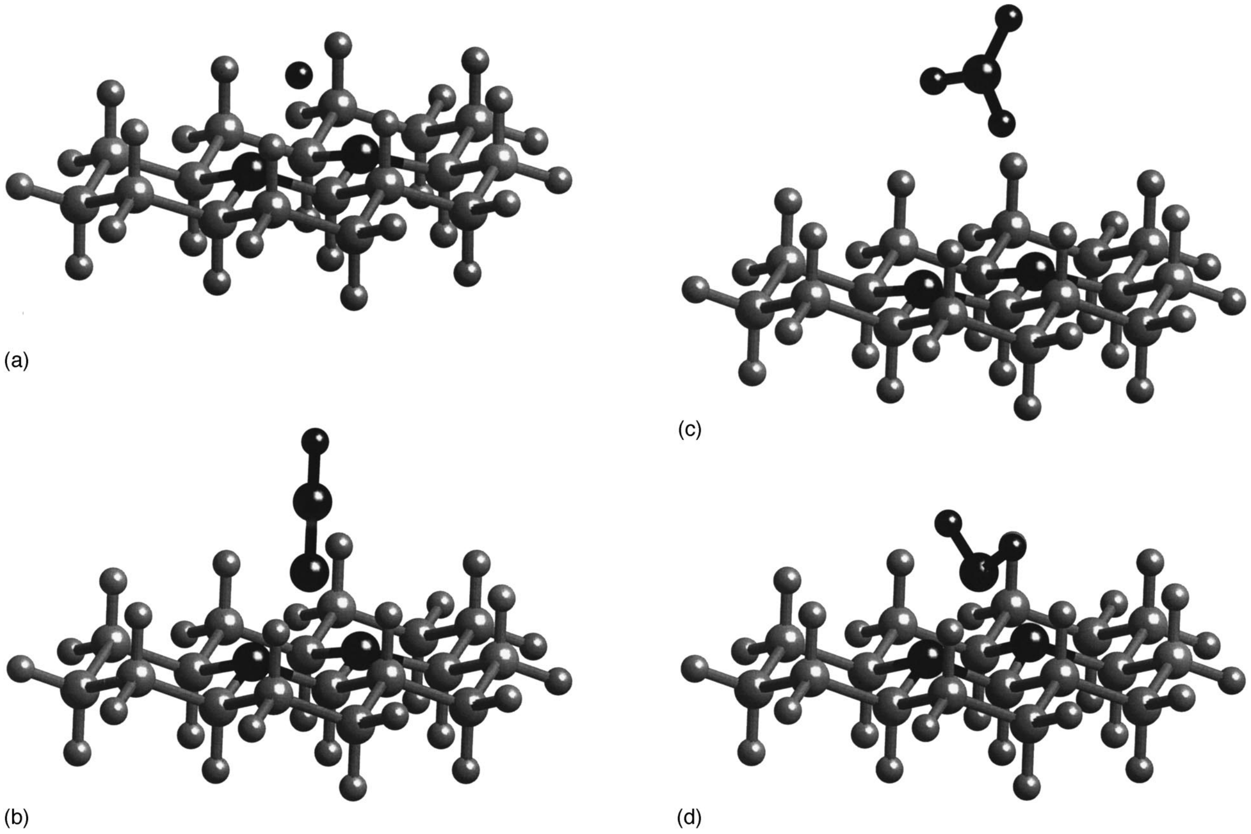

FIG. 1. Templates demonstrating the transition state for the migration of H (a), C_2H (b), CH_3 (c), and CH_2 (d), respectively, on a diamond (111) surface.

growth conditions. Migration of the chemisorbed species H, CH_3, CH_2, and C_2H, respectively, is then assumed to occur as a simple jump between the two identical radical surface sites on an otherwise H-terminated surface. The C_2H_2 species, however, is assumed to migrate by an alternating one- and difold site adsorption to the surface (Fig. 2).

The Schrödinger equations for the models of surface migrations were solved using the *ab initio* molecular orbital method at the second-order Møller-Plesset (MP2) of theory (Møller-Plesset perturbation theory of second order).[16] The migrating species, the radical surface atoms, as well as the closest carbon neighbors to the radical ones at the surface, were then represented by the basis set 6-31G**. This split-valence basis set is able to give an improved description of expansion or contraction of the valence shell in response to differing molecular environments. Furthermore, by adding polarization functions (*p* to H and *d* to C) the description of the charge rearrangement occurring around the atoms will be better. The remaining atoms were all represented by the much smaller basis set Slater-type orbitals-3G.

Migration barriers are normally more difficult to calculate than adsorption energies to a surface radical site, because of the problem of location of the transition state. Furthermore, calculation of migration barriers for large models is an extremely demanding computational task. An optimization to a transition state geometry, where the chemisorbed species as well as all uppermost atoms in the template modeling the diamond (111) surface are allowed to be fully relaxed (shown by filled circles in Fig. 1), is generally extremely memory and time dependent. In the present study, the transitions-state geometry was instead determined by varying one reaction coordinate in subsequent calculations, while the rest of the coordinates for the uppermost atoms were changed freely in each calculation. Other underlayer atoms

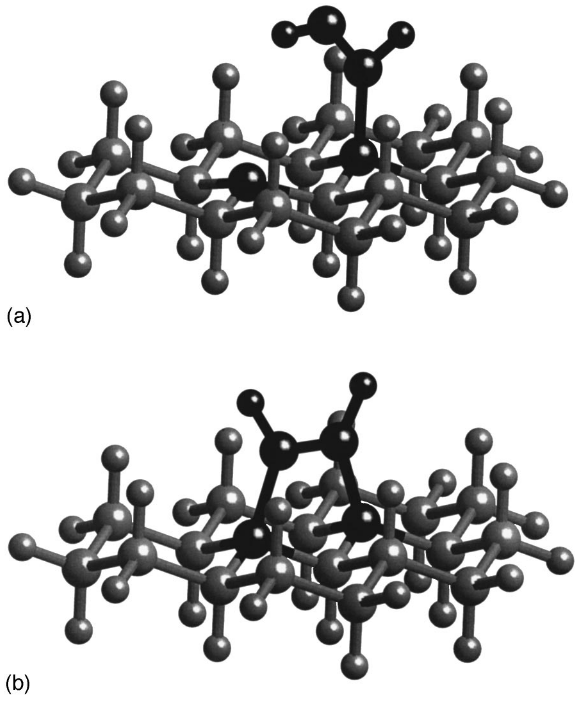

FIG. 2. Templates demonstrating the (a) onefold- and (b) difold-site bonding during migration of C_2H_2 on a diamond (111) surface.

were kept fixed in order to hold the characteristics of the crystal. The transition state on the potential energy surfaces, describing the energy path when going from the chemisorbed state to a transition state during the surface migration, was decided by the following procedure. First, the position of the projected transition state on the axis intersecting two chemisorbed species (adsorbed to the two neighboring radical surface sites) was determined by calculating a potential path along this very axis. The obtained potential energies were then least-squared fit to a parabola whose maximum was situated at the midpoint of this intersecting axis. Second, the more exact barrier for migration was obtained by performing a similar procedure, but perpendicular to the intersecting axis at the position of the first obtained potential-energy maximum. The above-mentioned atoms (adspecies and uppermost surface carbons) were also allowed to relax in the calculations of the adsorption energies for the chemisorbed state. The activation energy for a specific species and jump process was then calculated as the difference in energy for the transition state and the chemisorbed state.

III. SOURCES OF ERRORS

A. Introduction

Only relative energy barriers have been of any interest to study within the present investigation. The purpose was not to quantitatively make predictions regarding energy of barriers to any chemical accuracy (about 0.1 eV). However, the numerical differences for the different adspecies studied (>102 kJ/mol) were large enough in order to be able to predict a trend.

There are three possible sources of errors within the present work; (a) size and form of the template modeling the diamond (111) surface, choice of method for (b) electron-correlation correction, and (c) transition-state location.

B. Template size

As a check, a six-layer-thick slab with periodic-boundary conditions was used. Calculations were then performed using the program system CASTEP from Biosym/Molecular Simulation Technologies of San Diego. The approximation method used was the gradient corrected local-density aproximation version as developed by Perdew and co-workers.[17] The electronic wave functions were expanded using a plane-wave basis set and the electronic minimization was performed using a band-by-band conjugate-gradients minimization technique.[18] A plane-wave basis set with a cutoff energy of 400 eV was then used. The electron-ion interaction was described by using pseudopotentials, which were generated using the scheme of Lin,[19] ensuring the transferability of the potentials. The calculations were fully self-consistent with eigenvalues and was obtained using 1 k point, generated in the program according to the Monkhorst-Pack scheme.[20] This scheme produces a uniform mesh of k points in reciprocal space.

In the calculations, a supercell approach was used. The six-layer slab was included in a unit cell with vacuum regions of 18 Å in the (001) direction, while keeping the periodicity in the (100) and (010) directions. The size of the supercell in these latter directions were four and six carbons, respectively. The effect of size and number of atoms allowed to be relaxed, on the adsorption energy as well as on the barrier of energy, were then investigated for the migration of H species. It is generally known that adsorption of gaseous species to the diamond (111) surface is not especially size dependent due to the very localized covalent bonds. The present test calculations will then both varify this statement, as well as investigate if the same is true also for the energy barrier on the diamond (111) surface. As a result, a difference of less than 3 (2)% was obtained when calculating the barrier energy (adsorption energy) using the six-layer slab and the cluster presented above. A number of three layers of carbons were allowed to relax in the six-layer-thick slab, also including the surface terminating H atoms. Hence, a minor (and almost identical) improvement was obtained for both the adsorption energy, as well as for the barrier energy, at least concerning the purposes within the present paper.

C. Electron correlation corrections

Tachiba *et al.* have studied the fluorination process in thermal etching of a silicon substrate.[21] The barrier of energies for model reactions, describing the migration of F atoms, were then calculated. The electron correlation energies were estimated with the second- and third-order Mǿller-Plesset perturbation method (MP2 vs MP3), and with frozen-core single- and double-substituted configuration interaction (CISD) using the 6-31G** basis set. Unlinked cluster quadrupole correction (QC) was added to allow for size-consistency corrections (MP2, MP3 vs CISD-QC). For a specific model reaction, the energy barriers obtained by the CISD-QC method were numerically the largest ones, while the corresponding energies obtained by the MP2 method were numerically the smallest ones. The differences in energy barriers, using the MP2 and CISD-QC method, respectively, were within the range (17–21) kJ/mol. On the other hand, the differences in barrier of energies for the different model reactions were quantitatively almost identical for the methods of electron-correlation corrections used.

Moreover, the addition of CH_3MgCl to chiral α-alkoxy carbonyl compounds were investigated in a paper by Safont *et al.*[22] The PM3 semiempirical procedure and the *ab initio* method at HF level of theory with the 3-21G and 6-31G* basis sets were applied to identify the stationary points on the potential energy surface. The correlation effects were included by using the MP2/6-31G* method, as well as by means of MP3/6-31G*//MP2/6-31G* and MP4/6-31G*//MP2/6-31G* single-point calculations. The dependence of the results upon the computing method was analyzed. There were differences obtained on the barrier-height values. However, the tendencies were found to be similar. It has unfortunately been practically impossible to investigate the effect of an improvement in electron-correlation correction methods within the present investigation.

D. Transition-state location

As mentioned above, the migration of H on diamond (111) surfaces have earlier been investigated theoretically by Chang, Thompson, and Raff.[13] However, the bonded H species were then allowed to be translated horizontally from one adsorbed position on the surface to another. This translation is, in fact, identical with the first part of the procedure for transition-state location used in the present paper. The energy barrier obtained by Chang and co-workers for a migration between two adjacent carbon radical sites was 317 kJ/mol. This value is to be compared with our corresponding result of 283 kJ/mol. However, the true transition state is most probably not situated on the axis intersecting two chemisorbed species.

As will be discussed in Sec. IV, the transition state has also been localized by performing geometry optimization to a transition state. This was done in order to check the present method used for computation of migration barriers. A minor difference in barrier height (<8%) was then obtained. Hence, the present procedure used for locating the transition-state geometry was found to be accurate enough for the purposes within the present paper. As expected, the geometry of the transition state obtained for the migration of H is not situated at the line intersecting the adsorption sites. This is reflected in, e.g., the barrier of energy, which is, hence, appreciable smaller (by about 69 kJ/mol) compared to the energy reported in the paper by Chang, Thompson, and Raff. As a conclusion, the cluster approach, choice of method for electron correlation correction, and method for transition-state location, have been proven to be adequate for the purpose with the present paper.

IV. RESULT AND DISCUSSION

A. General

The migration process in the present investigation is assumed to involve two neighboring-surface radical sites. Migration of H, CH_3, CH_2, and C_2H, respectively, is then assumed to occur as a single jump between these two surface sites. The migration will be of an anisotropic character since every surface carbon has six symmetrically equivalent carbon neighbors on the surface (Fig. 1). The actual migration will, however, be determined by the formation of vacant radical sites by H abstraction. It has earlier been found theoretically that a onefold site adsorption of the C_2H_2 species to a radical site on an otherwise H-terminated diamond (111) surface is much weaker than a corresponding difold site adsorption to a diradical surface site (104 vs 451 kJ/mol).[23] Due to these observations, the C_2H_2 species will, in the present paper, be assumed to migrate by an alternating one- and difold site adsorption to the diamond (111) surface.

B. Migrating H species

The calculated migration barriers at the MP2 level of theory, as well as the energy for adsorption to a single radical site, are demonstrated in Table I. It is observed that the obtained order of the energy barriers for the single jump process is $CH_2<H<C_2H\approx CH_3$. These barriers are numerically smaller than the corresponding energies for adsorption (assumed to be the inverse of desorption). As can be seen in Table I, the energy obtained for migration of H is 248 kJ/mol, being about 200 kJ/mol lower than the energy of adsorption of H (441 kJ/mol). The potential energy change, following the migration from one chemisorbed position to another neighboring chemisorbed position, is shown in Fig. 3(a). The potential energy increases because of the bond dissociation of $C_{radical}$-H accompanying the adatom migration. The obtained potential energies were least-squared fit to a parabola whose maximum was situated at the midpoint of the potential path. This is the result of the migration of any of the adatoms H, CH_3, CH_2, and C_2H in the present paper. A similar maximum in potential energy is expected to be obtained if the adatoms are allowed to migrate perpendiculary to this previously obtained one in the plane of the surface.

TABLE I. Energy barriers for migration, as well as adsorption energies, for different species on the diamond (111) surface. The results are within the MP2 theory.

Migrating species	$\Delta E_{barrier}$ (kJ/mol)	$\Delta E_{adsorption}$ (kJ/mol)
C_2H	350	628
H	248	441
CH_2	52	416
CH_3	353	388
C_2H_3	186	72

The final transition state was then located by performing a similar procedure but perpendicular to the first obtained energy maximum [Fig. 3(b)]. The distance between the H species and a plane intersecting the majority of the surface carbons was varied in subsequent calculations, while the rest of the coordinates of the uppermost atoms (marked in Fig. 1) were fully relaxed. The geometry of this transition-state migration is shown in Fig. 1(a). The distance between the adatom H and one of the radical carbon atoms is 2.1 Å. To check the method of computing migration barriers, all of the uppermost atoms (as well as the adatom H) were allowed to be geometrically optimized in a search for a transition state. This was done within the density functional theory using the Becke exchange functional and the LYP correlation functional.[24] A migration energy of 270 kJ/mol was then received (a difference in barrier height of less than 8%).

Migration reactions of hydrogen H have earlier been theoretically investigated for the principal diamond surfaces; (111), (110), and (100).[4,8,10–14] Surface diffusion of H on diamond (110) has been studied by different quantum-mechanical methods.[11,12] H atoms were then found to migrate with an energy dependent on the path between neighboring sites, as well as dependent on different directions on the surface. It was found probable that diffusion within troughs between the {1-1 0} ridges (barrier energy of 200 kJ/mol) can occur within the lifetime of the surface radical site [60 us (Ref. 25) or 180 us (Ref. 12)]. In a paper by Frenklach and Skokov,[8] it was found that migration of H species on monohydrogenated (100)-(2×1) surfaces encounters large barrier energies (>51.1 kcal/mol), and therefore should not affect the distribution of surface radicals. The migration path with the lowest energy barrier on a (111) surface (322 kJ/mol) was found to be between two neighboring radical surface sites in a paper by Chang, Thompson, and Raff. Molecular dynamics and classical variational transition-state theory calculations were than performed, using the semiempirical hydrocarbon potential-energy surface developed by Brenner.[26] The results received for the corresponding migration of H in the present paper [248 (potential

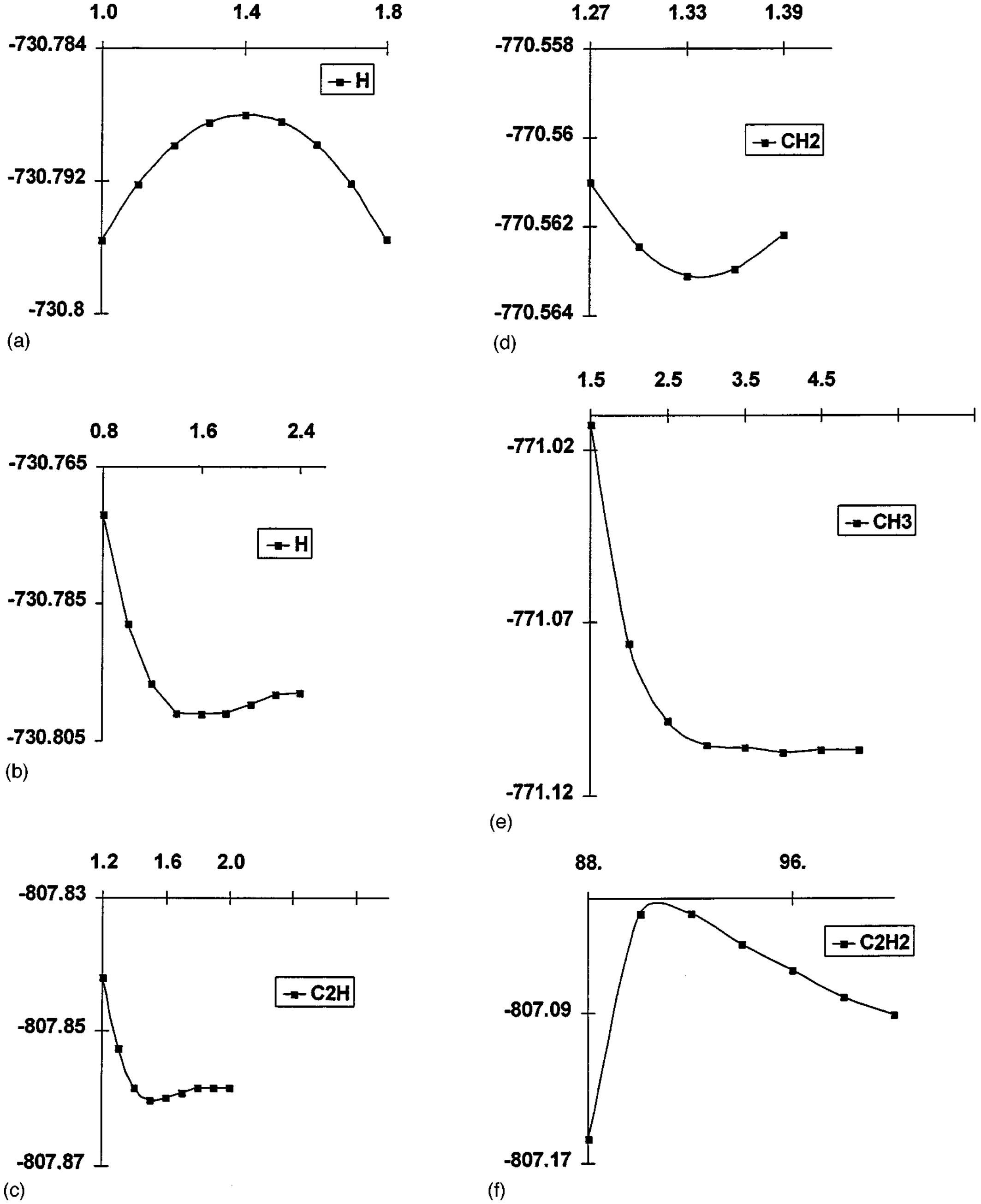

FIG. 3. Potential energy paths used for the determination of transition-state geometries for H (a) and (b), C_2H (c), CH_2 (d), CH_3 (e), and C_2H_2 (f). (b)–(e) demonstrates the potential path obtained when moving the species in a direction perpendicular to the surface, through an obtained potential maximum shown in (a) positioned due to symmetrical reasons more or less exactly inbetween the two surface diradical sites. The y axis in the figures are representing the calculated total energies of the systems. The x axis in (a)-(e) are representing the distances between the migrating species and a plane intersecting the surface carbons. The x axis in (f) is representing the angle formed by the surface carbon and the two C on C_2H_2 ($v_{\text{C-C-C surface}}$).

surface), 270 (transition state) (TS)] kJ/mol are in a reasonable agreement with the result obtained in the paper by Chang, Thompson, and Raff.[13]

C. Migrating C_2H species

As can be seen in Table I, the C_2H species has the largest tendency for adsorption to a monoradical diamond (111) surface (adsorption energy of 628 kJ/mol). It has also one of the largest barrier for migration (350 kJ/mol), preventing an adsorbed C_2H species to move more or less freely over the surface. The barrier of migration is, hence, considerably more energetically favorable (by about 280 kJ/mol) compared to any desorption process.

The transition state for migration of the C_2H species was located by performing a procedure identical to the one used in the case of H migration [Fig. 3(c)]. The geometry of this transition state is shown in Fig. 1(b). The distance obtained between the carbon atom in C_2H (bonded to the surface carbon in the chemisorbed state) and one of the radical surface carbons is 2.1 Å. The much larger barrier of migration for C_2H can be explained by the increase in C-C bond length in the C_2H species at the position of the transition state, compared to the corresponding bond length for a chemisorbed state (1.24 vs 1.19 Å). It is well known that the main part of the correlation energy comes from the electrons with opposite spins, since electrons with parallel spins are automatically kept apart because of the antisymmetry of the wave function. These effects are of special importance in triple bonds, e.g., C_2H species. The lengthening of this triple bond during migration ($\Delta_{max}=0.05$ Å) will result in a decrease in electron correlation, contributing to the large barrier of migration.

D. Migrating CH_2 species

As can be seen in Table I, the lowest energy barrier in the present investigation is obtained for the migration of the more stable triplet state ($^3B_1$) of CH_2 (52 kJ/mol). Single jumps of CH_2 between neighboring radical C sites, on an otherwise H-terminated diamond (111) surface, may then occur within the lifetime of the surface radical site [60 us (Ref. 26) or 180 us (Ref. 12)]. A CVD gas mixture, containing CH_2 as the carbon-containing species would, hence, be energetically ideal due to its large adsorption energy (416 kJ/mol) and high probability for surface migration.

The potential path used for location of the transition state for CH_2 migration is shown in Fig. 3(d). The geometry of this transition state is shown in Fig. 1(c). The distance obtained between the C atom in CH_2 and one of the radical surface carbon atoms is 2.0 Å. The geometry of the CH_2 species at the transitions state is not identical to the geometry for the chemisorbed state. The H-C-H angle for the transition state is about 120°, being less than 180°, which was the corresponding angle for the chemisorbed state. The calculations shows that the CH_2 species binds strongly to the surface at the geometry of the transition state. Two single bonds are then formed between the triplet state of CH_2 and each of the two radical surface carbons by overlapping dangling bonds.

Migration reactions of the CH_2 species have earlier been theoretically investigated for the (100) and (001) diamond surfaces. The CH_2 migration energy barriers in the presence of H vacancies on the monohydrogenated diamond (100) surface were calculated to be low enough for surface migration to occur under low-pressure diamond-growth conditions (174 and 183 kJ/mol in the [1-1 0] and [110] directions, respectively). Furthermore, Skokov *et al.*[7] showed that a dimer row on diamond (100) will serve as an attractor for the migrating CH_2 species. The migration of CH_2 towards the dimers were sufficiently irreversible. Surface migration of CH_2 species was also computed to be fast and nearly isotropic in both directions (along dimer chains and dimer rows) in a recent paper by Frenklach and Skokov,[8] the largest energy barrier obtained in the reaction pathway for the migration of CH_2 was 152 kJ/mol. The migration of the CH_2 species on a diamond (001) surface has also been investigated.[4] No migration was found to be possible without dangling-bond assistance. The barrier energy of the limiting step was found to be above 386 kJ/mol, disregarding the migration of CH_2 as a likely process on a (2×1) reconstructed C(001):H surface.

The energy barrier for the migration of the CH_2 species on a diamond surface has, hence, been shown to be numerically much smaller for a hydrogenated (111) surface (in the present of vacancies), compared to hydrogenated (100) or (001) surfaces. Surface migration of CH_2 on C(111):H should then be low enough to occur under low-pressure diamond-growth conditions.

E. Migrating CH_3 species

The adsorption energy of CH_3, and the barrier energy for the migration of CH_3, has been calculated to be almost identical (388 vs 353 kJ/mol) (Table I). In fact, the barrier of migration is the largest one obtained in the present investigation. Hence, the present results indicate an almost identical probability for desorption and migration to occur when energy is supplied to the system, for example, in the form of an increased temperature.

The potential energy path obtained when moving the CH_3 species towards the diamond (111) surface is shown in Fig. 3(e). A transition state was unexpectedly not found. The potential energy was found to be approximately constant for a distance between the C atom in CH_3 and one of the radical carbons atoms down to about 1.7 Å. When decreasing this distance further, the potential energy started to increase due to sterically induced repulsive interactions. The geometry of the model close to the position where the potential energy starts to increase is shown in Fig. 1(d). The distance obtained between the C atom in CH_3 and one of the radical surface carbons is 3.8 Å. Furthermore, the adspecies CH_3 was then found to be planar, with two of the H atoms in the directions of the two radical surface carbons. Hence, the plane of the CH_3 species was in parallel to the line intersecting the two radical carbons. The fully relaxed geometry of a single CH_3 species is also known to be planar, with 120° for each $v_{\text{H-C-H}}$. The difference in energy for a chemisorbed state to one of the radical surface carbons, and the potential energy calculated at the position where the energy starts to increase, is in the present paper regarded to be the barrier energy for the migration of CH_3. The geometry of the adspecies CH_3 during migration from one surface carbon to a neighboring one will then change from a bonding situation, where C in CH_3 is chemisorbed to the surface (and the geometrical form of CH_3 is more like an umbrella), to a barrier situation where the CH_3 species is planar with two H atoms directed towards the two surface-radical carbons, and then back again to the former type of bonding situation. The electron density obtained in the region between the migrating CH_3 and the radical surface-carbons species at the transition state, shows that there is no tendency for the migrating CH_3 species to be bonded to any of the radical surface carbons.

Migration reactions of the CH_3 species have earlier been theoretically investigated for the (100) diamond surface. The migration of the CH_3 species on radical sites of the monohydrogenated (100) surface has been investigated in a paper by Mehandru and Anderson.[9] Relatively high migration barriers of 251 and 261 kJ/mol were then calculated for CH_3 moving to adjacent vacancy sites along the {110} and {110} directions.

F. Migrating C_2H_2 species

It has earlier been found theoretically that the C_2H_2 species will chemisorb much more strongly to the hydrogenated diamond (111) surface by forming a difold-site bonding to a diradical surface site, compared to a onefold-site bonding to a single radical surface site (104 vs 451 kJ/mol). Hence, the following migrational path was suggested for the C_2H_2 species on an otherwise H-terminated diamond (111) surface. A C_2H_2 species is first assumed to undergo a onefold-site adsorption to the surface. When a neighboring radical site has been created by an abstracting reaction with a gas-phase species, the C_2H_2 species will bend over towards the neighboring surface radical carbons (Fig. 2). A second C-C bond will then be formed between the C_2H_2 species and this neighboring surface C. The migration is then assumed to continue by a bond breakage of the first created C(surface)-C(C_2H_2) bond, resulting in a onefold-site adsorption of C_2H_2 to the second radical-carbons atom.

The potential path describing the formation of a difold-site bond from a corresponding onefold-site bond is shown in Fig. 3(f). As can be seen in Table I the barrier energy obtained for this formation is much larger than the energy obtained for a onefold-site adsorption to the surface (186 vs 72 kJ/mol). Hence, desorption of a onefold-site chemisorbed C_2H_2 species would be energetically favorable compared to the assumed migration of C_2H_2 (by alternating onefold- and difold-site adsorption) on an otherwise H-terminated diamond (111) surface.

V. SUMMARY

Recent results have indicated that under conditions typical of diamond CVD surface migration will play a critical role in the deposition process.[27–29] Migration of various important CVD species (H, CH_3, CH_2, C_2H, and C_2H_2) on a diamond (111) surface has been investigated theoretically in the present paper using a cluster approach and the second-order Mǿller-Plesset perturbation theory. The migration of the chemisorbed species H, CH_3, CH_2, and C_2H, respectively, is then assumed to occur as a simple jump between two neighboring (and identical) radical surface sites on an otherwise H-terminated surface. The dangling bonds are assumed to be created by abstraction reactions including species in the gas phase. These types of surface vacancies are assumed to exist under low-pressure growth conditions. It is observed that the obtained order of the energy barriers for the single jump process is $CH_2 < H < C_2H \approx CH_3$ (52, 248, 350, and 353 kJ/mol, respectively). These barriers are all numerically smaller than the corresponding energies for adsorption (assumed to be the inverse of desorption) (416, 441, 628, and 388 kJ/mol, respectively). The energy differences are, with one exception, within the (193–364) kJ/mol range. The adsorption energy of CH_3, and the barrier energy for the migration of CH_3, has been calculated to be almost identical (388 vs 353 kJ/mol). In fact, the barrier of migration is the largest one obtained in the present investigation. The smallest energy barrier in the present investigation is obtained for the migration of the more stable triplet state ($^3B_1$) of CH_2 (52 kJ/mol). One explanation is the fact that the present calculations show that no tendency was observed for the CH_3 species to be bonded to the diamond, while the CH_2 species was found to be strongly bonded to the surface at the transition state. These results suggests that the chemisorbed CH_2 species is likely to more mobile than CH_3 at diamond-growth temperatures.

The C_2H_2 species is in the present paper assumed to migrate by an alternating onefold- and difold-site adsorption to the diamond (111) surface. The barrier energy obtained for the first part of this migration process is much larger than the energy obtained for a onefold-site adsorption to the surface (186 vs 72 kJ/mol). Hence, desorption of a onefold-site chemisorbed C_2H_2 species would be energetically favorable compared to the assumed migration of C_2H_2. Even regarding the possible sources of error in our calculations, the results in the present investigation makes it possible to diminish the role of C_2H_2 as a dominating growth species for any surface process largely based on surface migration on diamond (111) surfaces. However, an excess of CH_2 species in the gas mixture in a CVD process would be energetically ideal due to its large energy of adsorption and high possibility for surface migration on diamond (111).

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