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Epitaxial Growth Mechanism of Diamond Crystal in CH_4–H_2 Plasma

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Abstract: Quantum chemical calculations were carried out in order to elucidate the mechanism of the astonishing observation that diamond crystal can be synthesized in a low temperature CH_4–H_2 plasma at a pressure of a few torr. A most probable mechanism was found to proceed in two steps, i.e., first, covering the (111) plane of the diamond surface by methyl groups, and second, epitaxial growth, where the three neighboring methyl groups standing on the (111) plane of the diamond surface are spontaneously bound to form the diamond structure via methyl cation intermediates. Detailed atomic displacements during the above reactions are shown to obtain a realistic understanding of the mechanism.

Chemists have believed that synthetic diamond can only be produced under ultrahigh pressure (70000 Kg/cm^2) at very high temperature (2300 K) from graphite by the help of a catalyst.[1] However, recent experiments in many laboratories show that small crystals or thin films of diamond are formed under a few torr of pressure in a low-temperature hydrogen plasma which contains a small amount of methane.[2] This is an astonishing observation, and the mechanism remains obscure.

Since no phase transition of graphite or amorphous carbon takes places under the conditions of low-temperature plasma reaction, the diamond formation in vacuum is considered to proceed by chemical reactions, different from the phase transition of graphite under ultrahigh pressure at very high temperature. Then, how and by what kind of chemical species does the growth of diamond surface occur in this plasma atmosphere? This paper describes a most probable mechanism of the epitaxial growth of diamond crystal, which was elucidated by the method of quantum chemical calculations.

Since the plasma used for diamond synthesis contains mainly hydrogen with just a few percent of methane, only hydrogen molecules may react with radicals and ions which are produced by the dissociation of methane. The contribution of methane molecule in this stage will be negligibly small. So, the chemical species produced in the CH_4–H_2 plasma are CH_4^+, CH_3^+, CH_2^+, CH^+, C^+, H^+, H_2^+, CH_5^+ and H_3^+ as well as CH_3, CH_2, CH, C, and H. These active species can react with the surface of diamond crystal.

However, provided that these active chemical species simply react at random with the surface of diamond crystal, no diamond growth will occur, and the products will be highly crosslinked polyethylene or amorphous carbon. For example, if a singlet methylene radical (CH_2) inserts itself into the C–H bond of diamond crystal surface, the product is $>C{-}CH_3$. And if this reaction repeats, highly branched polyethylene but no diamond will be produced. Therefore, a specific reaction which is strictly oriented and spontaneously produces the crystal growth of diamond must be responsible for the observed growth. This paper discusses our search for such a reaction process or processes.

Table I. The Reaction $>C{-}H \rightarrow >C{-}CH_3$

A. Methylene Insertion

$>C{-}H + {}^1CH_2 \rightarrow >C{-}CH_3$

B. Hydrogen Abstraction + Methyl Radical Addition

$>C{-}H + {}^2H \rightarrow >C\bullet + H{-}H$

$>C{-}H + {}^2CH_3 \rightarrow >C\bullet + HCH_3$

$>C{-}H + {}^3CH_2 \rightarrow >C\bullet + {}^2CH_3$

$>C{-}H + {}^2CH \rightarrow >C\bullet + {}^1CH_3$

Then, $>C\bullet + CH_3 \rightarrow >C{-}CH_3$

Method

Quantum chemistry provides a method to determine a unique reaction route which follows the lowest energy path on the $3N - 6$ dimensional potential energy hypersurface, where N is the number of atoms constructing the reacting system. If the potential energy always decreases following the reaction path, the reaction is considered to take place spontaneously. Therefore, the quantum chemical method is a powerful tool for finding a reaction that proceeds spontaneously in one step and leads to the epitaxial growth of diamond.

Determination of the Lowest Energy Path. Since the plasma reaction system is very complicated, many possible reaction courses arise, some of which may not produce the epitaxial growth of diamond. In such an ambiguous situation, the calculation of the IRC (Intrinsic Reaction Coordinate) is able to confirm whether the reaction considered gives diamond spontaneously because it precisely determines the positions of all the atoms of the reaction system from the starting point to product formation following the lowest energy path. The IRC is defined as the lowest energy path connecting a reactant and a product through the saddle point (the transition state) on the $3N - 6$ dimensional potential energy hypersurface.[3] For simplicity, the IRC calculation were done on the mass-weighted 3N dimensional hypersurface. Then, the results were revised in such a manner that the center of mass and the three kinds of principal axes of inertia in a structure of the reaction system were always fixed on the IRC path. Starting from the saddle point, the IRC path was determined point by point following the procedure proposed by Ishida, et al.[4]

Geometry Optimization. A systematic method was applied which overcomes the difficulty of finding the stable and the transition state (TS) structures of the reaction system on the multidimensional hypersurface. The details of the method were published elsewhere.[5] By this method, we can easily obtain minima, the stable structures, and the saddle point, the transition state structure, by using the first and the second derivatives of the potential energy with respect to the structure change for the determinations of the former and the latter points, respectively.

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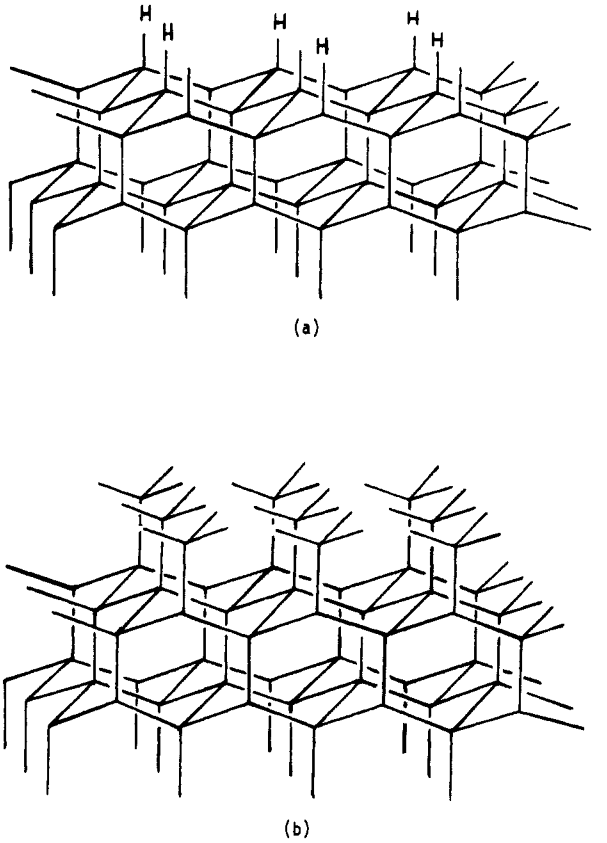

Figure 1. The (111) plane of diamond surface: (a) covered with hydrogens and (b) covered with standing methyl groups.

For the potential energy calculation, MINDO/3[6] level semiempirical molecular orbital calculations were used because ab initio MO calculations are impossible for such large reaction systems as considered here even in the case of a minimal basis set. Lischka studied the energy calculation of carbocations by an ab initio method with configuration interaction and concluded that MINDO/3 results are in good agreement with the inclusion of configuration interaction for a pure hydrocarbon system.[7] Lipkowitz also reported that MINDO/3 results reproduce the experimental data of σ-allyl cation isomers qualitatively.[8] Therefore, the results obtained in the present calculations will be reliable at least qualitatively.

Model Reaction of the Epitaxial Growth of a Diamond Surface

Quantum chemical calculations need an adequate model compound when such a large molecule as diamond crystal is studied. The model compound should reflect the properties of the diamond surface. Let's consider the (111) plane of a diamond surface. In a hydrogen plasma the (111) plane will be covered with hydrogen as shown in Figure 1a. To obtain diamond crystal growth, carbon atom deposition must take place in the next step. There are many reactive species containing one carbon atom in the CH_4–H_2 plasma used for diamond synthesis as already discussed. The one-carbon reactive species will convert the hydrogen which covers the (111) plane of the diamond to a methyl group. There are many reactions which will then change the $>$C—H group to $>$C—CH_3 as shown in Table I.

After a part or all of the diamond surface is covered by methyl groups as shown in Figure 1b, crystal growth may take place if three neighboring methyl groups are bound. The binding reaction of the three methyl groups should be accomplished by the attack of one reactive species because if the reaction takes place by a sequence of many reactive species the most probable product is not diamond but branched polyethylene. The reactive species effective for the diamond synthesis may not be a free radical but an ion, because an ionic species always produces a new ion after reacting with the first methyl group. The newly formed ion is then able to attack a second methyl group (Figure 2) to produce a more stable secondary cation and so on until reaction with all adjacent methyl groups is complete. We first examined the reaction of a methyl cation with methyl groups on the diamond surface.

Table II. Energy Difference between Each Intermediate in the Process of Diamond Synthesis[a]

model	S	L
ΔE_1[b]	126.34	130.97
ΔE_2[c]	68.57	66.07
ΔE_3[d]	16.56	17.97

[a] (kcal/mol by MINDO/3). [b] ΔE_1 = structure I − structure XII. [c] ΔE_2 = V − XII. [d] ΔE_3 = IX−XII. See Figures 2 and 3.

A model compound adopted for the calculations which determine the lowest energy path on the $3N - 6$ dimensional hypersurface is shown in Figure 2, where the model L has the smallest subunit structure of a diamond crystal, and the model S has only the surface structure of a diamond covered with methyl groups. In preliminary research, the large models L were used for energy calculation of structures I, V, IX, and XII in Figure 2. However, the energy differences between each of the intermediates are reproduced well, even when the smaller model S is adopted as shown in Table II. Thus, the small model S was used for the detailed calculations of the potential energy hypersurface shown in Figure 3.

Comparing Figure 2 with Figure 3, we can observe that the overall reaction proceeds in one step releasing a hydrogen molecule in each of three substeps, and the reaction site always retains the carbonium ion structure.

Throughout all of the calculations of Figures 2 and 3, the diamond structure of the model compound is kept invariant. The carbon atoms of the three standing methyl groups are allowed to displace in the Z-direction only (Figure 2). No limitation is applied for the displacement of all the atoms of the attacking methyl cation and all of the hydrogen atoms belonging to the three standing methyl groups.

The Lowest Energy Path of the Model Reaction

The detailed potential energy changes following the reaction path are shown in Figure 3. The reaction route is the lowest potential energy path. It is clearly shown that the reaction which binds three neighboring methyl groups proceeds spontaneously in one step when a methyl cation attacks one of the three methyl groups. A small activation energy of 6 kcal/mol is required at the first saddle point III but such a small activation energy will be supplied by the kinetic energy of the methyl cation incident from the plasma.

Suppose that a methyl cation approaches one of the three neighboring methyl groups on the diamond surface and that the carbon atom A of the methyl cation attacks one of the hydrogen atoms belonging to the methyl group and forms metastable intermediate II. In an actual reaction, the saddle point structure III may be formed directly with no formation of the intermediate II for once the metastable intermediate II has been produced, the reaction may stop since the activation energy required for passing over the saddle point III must be supplied from other uncertain origins. At the saddle point structure III, the C–C bond between the attacking methyl cation and the methyl group attacked is being formed, and the H–H bond between the eliminating hydrogen atoms is also being produced, but no liberation of the hydrogen molecule occurs in this step. The C–C bond is nearly complete at intermediate IV. Then, intermediate V, a bridged methylene cation $-CH_2^+-$, is formed in such a concerted process that carbon atom A originating from the methyl cation attacks a hydrogen atom of a second neighboring methyl group releasing the produced hydrogen molecule from the carbon atom A itself. Since a simple

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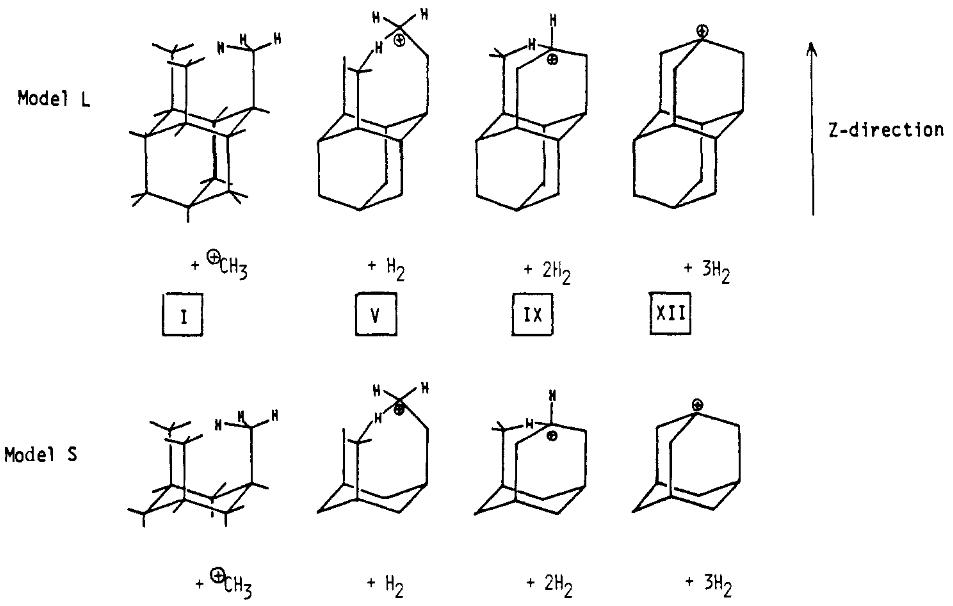

Figure 2. Model compounds: the notations I, V, IX, and XII are consistent with those in Figure 3.

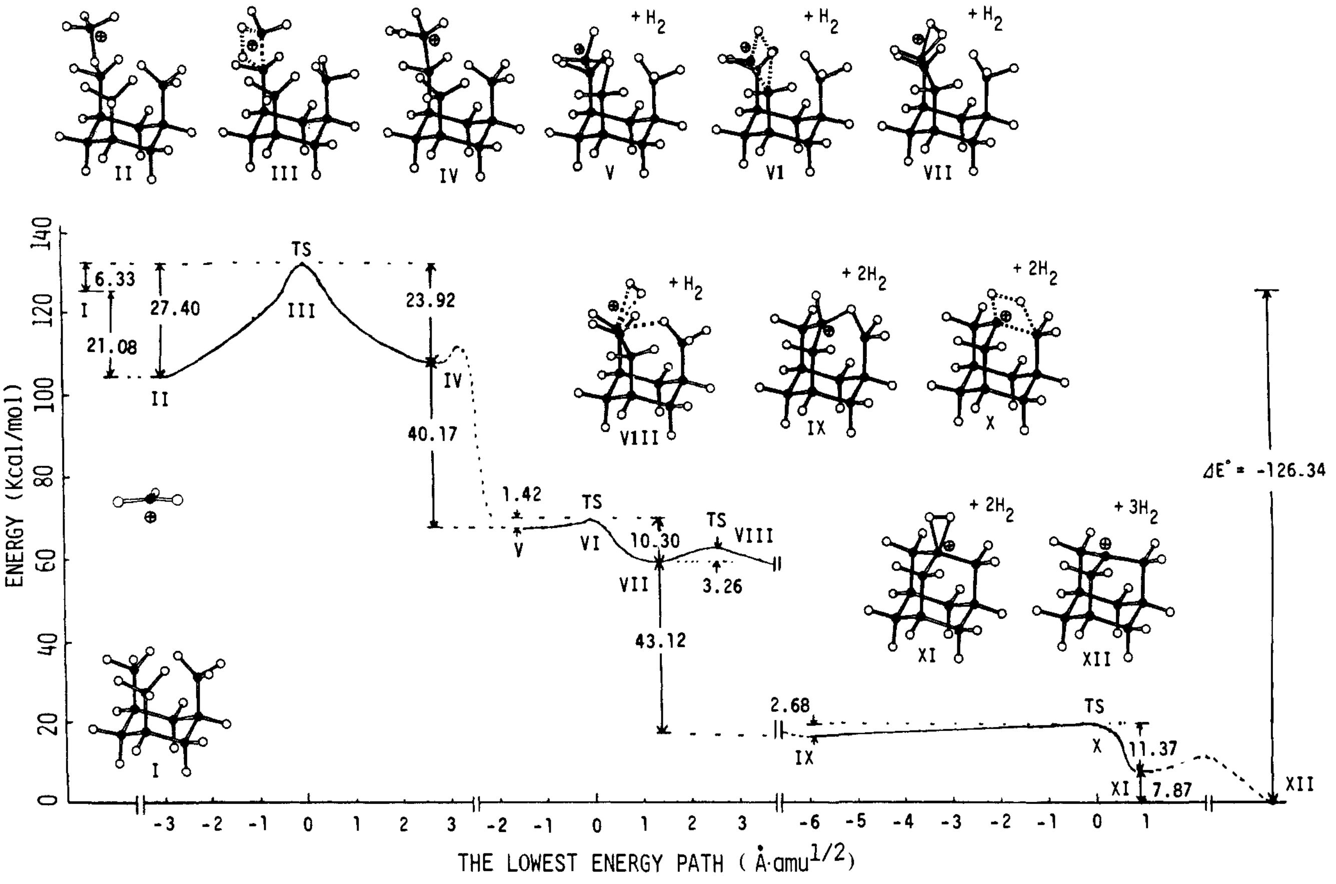

Figure 3. Detailed potential energy change following the reaction path of epitaxial growth of diamond surface. All structures of the reaction system are shown corresponding to the TS and the minimum point. Numerals are the energy difference in kcal/mol. Ordinate: potential energy in kcal/mol. Abscissa: the lowest energy reaction path in the mass-weighted $3N - 6$ dimensional Cartesian coordinate system (scale: Å·(atomic mass unit)$^{1/2}$. ●, carbon atom; O, hydrogen atom.

liberation of the hydrogen molecule from carbon atom A requires larger activation energy than the concerted mechanism, a nonbridged methylene cation CH_2^+–CH_2–ring which easily isomerizes to an ethylidene cation CH_3–CH^+–ring will not be produced.

The detailed displacements of atoms following the reaction II → III → IV are shown in Figure 4a, for the sake of a more realistic understanding. The similar pictures following the reactions V → VI → VII and VII → VIII → IX are shown in Figure 4 (parts b and c), respectively.

The reaction VI → VII → VIII → IX proceeds in the same fashion that the reaction III → IV → V does; i.e., at the saddle point VI, the C–C bond between the second methyl group and carbon atom A originating from the methyl cation and the H–H bond of hydrogen molecule to be eliminated are formed in the same process as at the first saddle point III. The C–C bond between the carbon atom A from the methyl cation and the second methyl group has been completed at intermediate VII. Then, intermediate IX is produced via such a concerted process that the

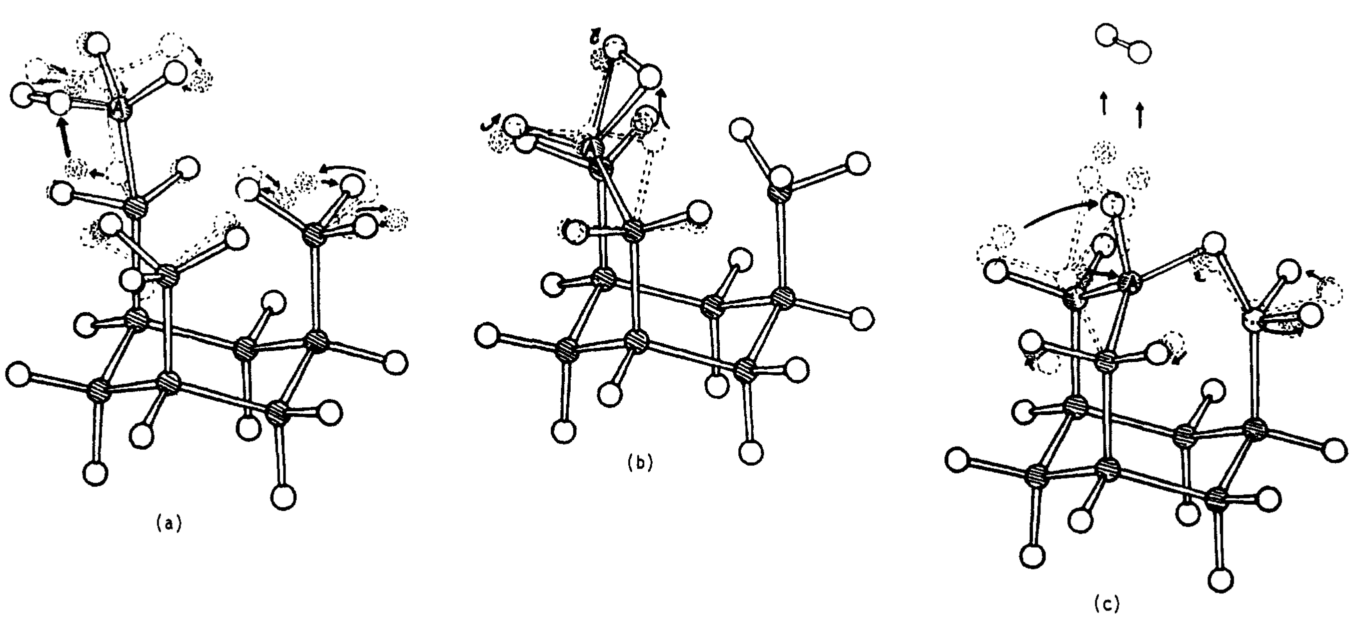

Figure 4. Detailed displacement of atoms following the reaction of epitaxial growth. The reactions proceed in the order ◌ (the starting minimum) → ◍ (the saddle point) → ○ (the final minimum): (a) II → III → IV; (b) V → VI → VII, and (c) VII → VIII → IX. The shaded circle ⊘ shows carbon atom in final minimum.

carbon atom A attacks a hydrogen atom of the remaining neighboring methyl group and releases a second hydrogen molecule at same time.

The reaction X → XI → XII also proceeds in a similar way. At the saddle point X, carbon atom A forms a bond with the carbon atom of the third methyl group. Following energy stabilization, the diamond structure is formed as shown in the structure of the intermediate XI. In the actual reaction, a third hydrogen molecule will be spontaneously released, and the final structure XII may be produced directly. Obviously the product XII has the diamond structure.

Discussion

Recent research revealed that SiH_3 radical is responsible for the formation of amorphous silicon (a-Si:H) in an SiH_4–H_2 plasma.[9] The result is in good agreement with the present research on CH_4–H_2 plasma, because the random deposition of CH_3 radical on solid surface always produces highly crosslinked polyethylene. It is also known that a-Si:H includes microcrystals of silicon. Since silicon takes the tetrahedral structure as its only stable form, a part of a-Si:H may automatically change to a microcrystal of silicon by annealing. On the other hand, carbon has two stable structures, i.e., diamond and graphite. Crosslinked polyethylene never changes to diamond but always to graphite by annealing.

We can imagine some examples of the multistep reactions for diamond synthesis where many radical species produced in a CH_4–H_2 plasma may contribute. But the probability of diamond formation by such a sequence of reactions will be very small or negligible because of the random nature. Since the ionic reaction mechanism found in this paper is not a random process and is strongly oriented toward diamond formation, we propose that this mechanism is most probable for diamond synthesis in a low-temperature plasma atmosphere, although other mechanisms are not excluded. Experimental support of this theoretical conclusion is the observation of the epitaxial growth of diamond on the (111) plane of natural diamond by Setaka and his co-workers.[2d]

Conclusions

The growth mechanism of a diamond surface in a reducing hydrogen plasma found in this study is as follows: the (111) plane of diamond surface is first covered by methyl groups (Figure 1). Then, the three neighboring methyl groups are bound spontaneously in one step by the single attack of a methyl cation. The same reaction occurs at other places on the surface. By repeating the chain of reactions, the epitaxial growth of the (111) plane takes place.

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Registry No. Diamond, 7782-40-3; methane, 74-82-8.

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