

Studies of Epitaxial Growth Mechanism of Diamond(001)

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Homoepitaxial growth mechanism of diamond(001) from gas phase was studied. By means of scanning tunneling microscope observation of an epitaxially grown surface, the diamond growth reaction site was found to be the S_B steps comprising carbon dimer row. Temperature dependence of the epitaxial growth rate on diamond(001) was experimentally investigated by hot-filament-assisted chemical vapor deposition. Tendency of growth rate was varied with distance between filament and substrate, and the apparent activation energies of surface reaction was estimated from the tendencies as 26-47kJ/mol at substrate temperatures between 440 and 1000°C. Calculations of reaction energy barriers of four kinds of one-carbon radicals on assumed growth site on the diamond(001) surface were also carried out by the molecular orbital method, and the values distributed between 0-53 kJ/mol were obtained. From these studies, diamond growth were considered to be contributed by many competitive carbon radicals and the dominant precursors and reactions were presumed to depend on growth conditions.

1. INTRODUCTION

Understanding of diamond growth mechanism from gas phase is imperative for application of both polycrystalline and epitaxial diamond films. Surface reaction models of CVD diamond growth which specified one- or two-carbon radicals as the staple precursor were proposed [1-5]. On the other hand, kinetic modeling which included both vapor phase reactions and surface reactions of many kinds of radical species were studied [6-7]. These kinetic simulations used the surface reaction rate coefficients, the mass of the coefficients were experimentally examined and others were calculated.

The apparent activation energies of diamond growth were experimentally investigated on both epitaxial [8] and polycrystalline [9] films.

Diamond(001) surface was proposed to be most preferable for high quality homoepitaxial growth [10]. Scanning tunneling microscopic (STM) observation of epitaxial grown diamond (001) with atomic scale resolution showed the atomic structures comprising 2x1 and 2x1 dimer rows. The observed structures suggested that the growing site of diamond(001) was comprised mostly S_B steps, and simulation of the surface reactions based upon actual molecular structures became possible.

2. EXPERIMENT

Homoepitaxial growth was performed on type Ib synthetic single crystalline diamond substrates by either 2.45GHz microwave-plasma-assisted CVD (MP-CVD) or hot-filament-assisted CVD (HF-CVD) from a methane-hydrogen gas mixture. $[\text{CH}_4]/[\text{H}_2]$ were in the range of 0.5% to 6.0%. The concentration was mainly 6% in MP-CVD and mainly 1% in HF-CVD. The gas pressure was 60Torr and the total gas flow was 200sccm in MP-CVD or 500sccm in HF-CVD.

After the growth, the samples were moved through the air to an estimating apparatus. STM observation was performed mainly in the air but also in high vacuum (10^{-9} Torr). Reflection high energy electron diffraction (RHEED) was also investigated.

Temperature dependence of the growth rate and RHEED patterns were investigated after growth by HF-CVD shown in Fig. 1.

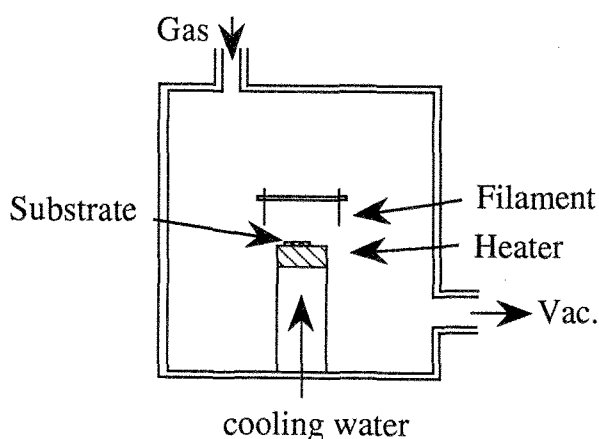


Fig. 1. Schematic diagram of HF-CVD apparatus.

In the growth conditions, the methane concentration in hydrogen and total gas flow were 1% and 500sccm and the filament temperature was 2200°C whose distances to the substrate were 8mm and 4mm. The substrate temperature were varied between 440°C to 1000°C. The substrate temperature was controlled by heater and water cooling and monitored by a sheathed thermocouple and a spot-welded one. The growth rate was estimated after 1 hour growth and after removing the molybdenum mask and measuring the thickness of selective film growth at the step.

3. RESULTS AND DISCUSSION

3.1 Atomic structure of epitaxial surface

The typical atomic scale STM image of epitaxially grown diamond (001) surface from methane 6%-hydrogen mixture at 830°C by MP-CVD is shown in Fig. 2(a). Almost identical STM images as those grown by HF-CVD at 830°C were obtained and also by STM observation in high vacuum (10^{-9} Torr). Parallel rows which were considered to comprising dimers of monohydride carbon were found all over the epitaxial surface. The reconstructed structure of epitaxial surface was also confirmed by RHEED [10].



Fig. 2. STM image of epitaxial diamond(001) surface.

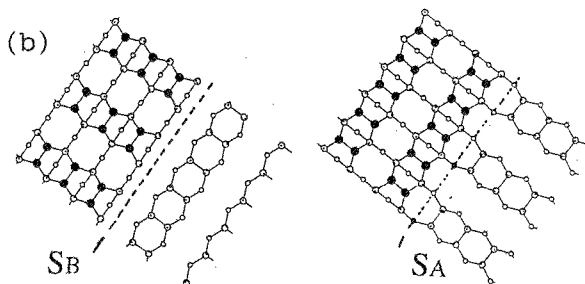
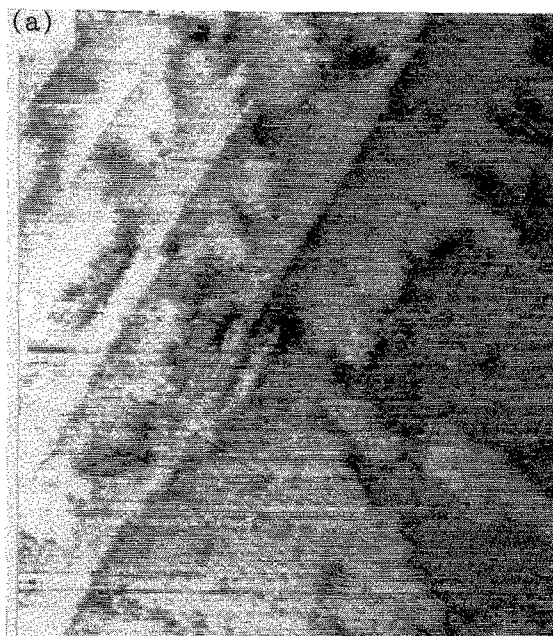


Fig. 3. (a) STM image of step formation on epitaxial diamond(001) surface. (b) Schematic drawing of S_A and S_B steps.

The STM image of lower magnification shown in Fig. 3(a) indicated the anisotropic step formation at S_A step and S_B step. It was considered from the step shapes that diamond crystal epitaxially grew at the front of the S_B steps by the extension of dimer rows after the nucleation. The most significant growth point of diamond(001) surface

was speculated to be the end of the dimer row.

3.2 Temperature dependence

The temperature dependence of the growth rate and RHEED patterns were studied. All epitaxial samples for this estimation were grown by HF-CVD from gas mixture including 1%-methane.

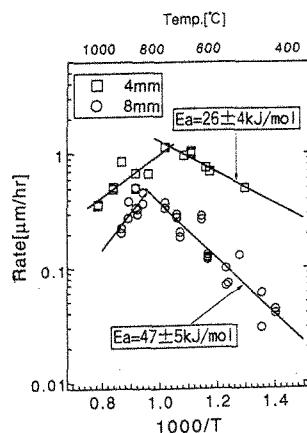


Fig. 4. Temperature dependence of growth rate on diamond(001)

Arrhenius plottings of the growth rate of epitaxial films synthesized by two kinds of filament distances 8mm and 4mm are presented in Fig. 4. The growth rate increased remarkably with the substrate temperature below 800°C , suggesting that the growth rate was controlled by surface reaction. Apparent activation energies (E_a) of surface reactions were calculated from the tendency of the plots in lower temperature. E_a for the 8mm-filament-distance condition was $47 \pm 5 \text{ kJ/mol}$, and that for 4mm was $26 \pm 4 \text{ kJ/mol}$. The differences of the E_a 's in diverse conditions was supposed to be caused by the variation in the relative amount of radicals with the filament distance.

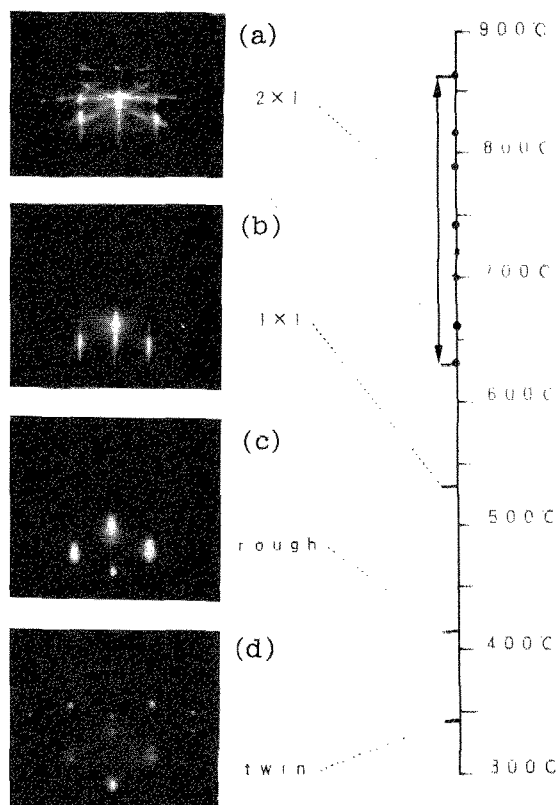


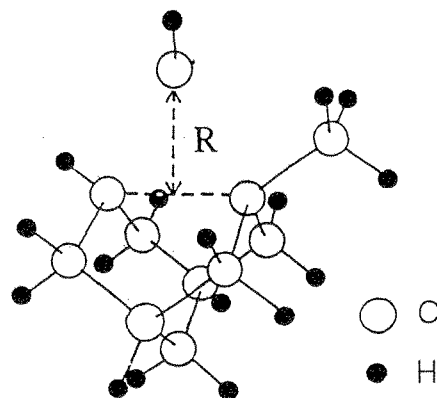
Fig. 5. RHEED Patterns of epitaxial diamond (001) at temperatures (a) 790°C, (b) 530°C, (c) 420°C and (d) 340°C

RHEED patterns of the films which were grown in the temperature range of 340°C to 870°C are shown in Fig. 5. In the temperatures higher than 600°C, RHEED diffraction patterns were sharp and streaky and significant peculiarities of 2x1 and 1x2 structures were found. In the temperatures lower than 600°C RHEED patterns became broad and spotty, and signals from the reconstructed structures became weak. This investigation indicated that the qualities of epitaxial films grown at higher temperatures were better than those of films grown at temperature lower than 600°C. Therefore, the 2x1 reconstructed structure was specific

to the high quality epitaxial film, and the dimer-row-extension mechanism were considered to be necessary for perfect diamond growth from gas phase.

3.3 Calculation of barrier energies

The cluster model of diamond surface for the energy barrier calculations was constructed by extracting from the structure of the top of the dimer row. Potential energy changes with the distance R between the cluster model and a kind of one-carbon radicals C, CH and CH₂ were calculated as the total heat of formation (Fig. 6). All calculations were carried out by the semiempirical molecular orbital method PM3 [11] in MOPAC6 on a SUMISTATION SS-300 workstation. The calculated potential curves plotted on the distance R (Å) are shown in Fig. 7(a,b,c). The energy barriers and the heat of reactions for each radical were 0 to 53kJ/mol shown in table.1.



R : C-C (radical) distance (Å)

Fig. 6. Reaction model of cluster and radical.

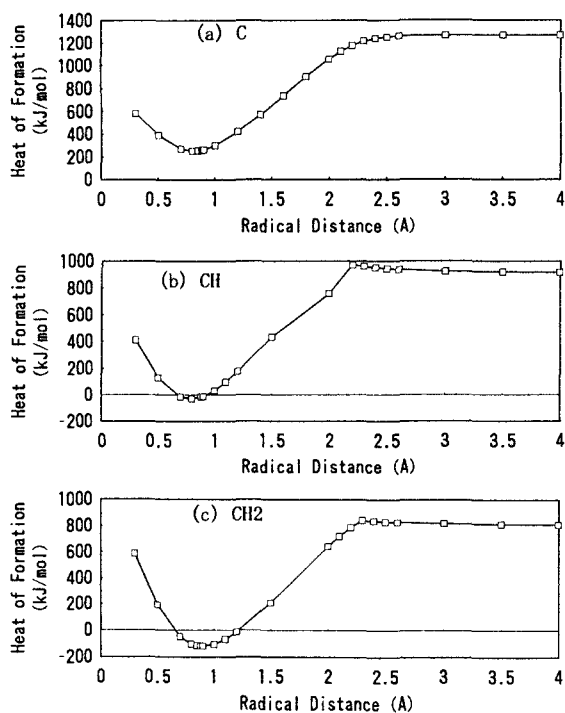
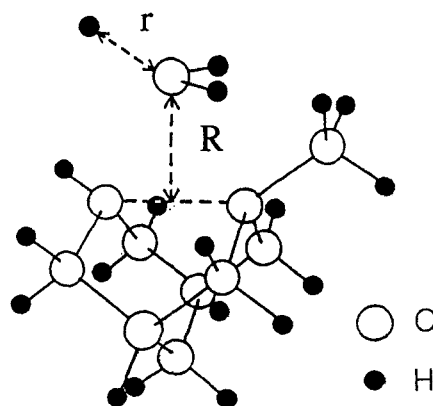


Fig. 7. Potential curves of reactions with (a) C, (b) CH, (c) CH₂.

In respect to the reaction of CH₃ radical with the cluster, it was necessary to extract the superfluous hydrogen atom. Two axis R and r of degree of freedom were assumed in order to simplify the simulation (Fig. 8). First axis R was for distance between the carbon atom of the radical and the center of the cluster the same as that of previous radicals. Second axis r was for the distance between the carbon atom of the radical and the superfluous hydrogen atom. Potential energies were calculated according to two axis and 3-dimensional plotting of the total heat of formation was obtained as in Fig. 9. For the precise estimation of barrier energy, determination of the transition state of the reaction of CH₃ was attempted based upon the molecular structure at the saddle point in Fig. 9.



R : C-C (radical) distance (Å)
r : C-H (radical) distance (Å)

Fig. 8. Reaction model for CH₃ and cluster.

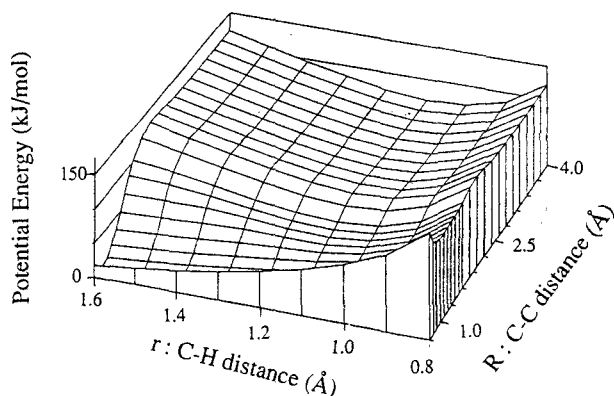


Fig. 9. Potential surface of reaction with CH₃.

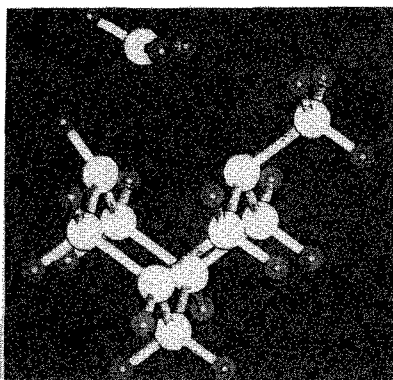
The transition state was successfully obtained for CH₃ reaction with the option TS of MOPAC6 as the structure in Fig. 10 and the barrier energy in the transition state was 23.9 kJ/mol.

Radical	C	CH	CH ₂	CH ₃
Point of Max Energy (Å)	—	2.2	2.3	2.2
Point of Min Energy (Å)	0.8	0.8	0.9	0.9
Energy Barrier (kJ/mol)	0	53.0	35.7	23.9 *
Heat of Reaction (kJ/mol)	-1016	-949	-924	-170

* Transition State

Table 1. Results of calculation

The reaction barrier energies of C₁H_x (x=0-3) radicals and the cluster calculated above were 0 to 53kJ/mol. All reactions with one-carbon radicals incorporated in the diamond are considered to be present on the assumed site at temperatures higher than 600°C. The apparent activation energies estimated by experiment were 26 to 47kJ/mol, and are within the calculated barrier energies. Many incorporating reactions with various kinds of radicals with diamond surface as well as those calculated above were speculated to be actually present in proportion to their relative amount in the gas phase.

Fig. 10. Structure of transition state with CH₃.

4. SUMMARY

The epitaxial growth site on diamond (001) was specified by atomic scale STM observation. Apparent surface activation energies of diamond(001) homoepitaxial growth were experimentally estimated. From temperature dependence of RHEED patterns, the high quality diamond(001) epitaxial film was elucidated with growth by dimer extension mechanism. The calculations of the surface reaction of carbon incorporation on the cluster model were carried out with respect to all C₁H_x (x=0~3) radicals by the semiempirical molecular orbital method PM3. Many kinds of surface reactions were expected to be available and competitive.

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