

A Model Calculation of Step-Flow Growth on Single-Layer Stepped Diamond (001) Surface

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Abstract: Step-flow growths of diamond on single-layer steps of hydrogenated diamond (001) surface have been investigated using the semiempirical molecular orbital method PM5. The chemical reactions at the first stage of growth have been calculated as a function of the charges biased to the substrates. When the frontier orbitals of a pair of surface hydrogen atoms of step edge by negative charge -2 interact effectively with frontier orbitals of hydrogen gases, the pair of surface hydrogen atoms is abstracted by two hydrogen gases. A dimer C_2 is bonded onto the pair of vacant hydrogen sites by the chemisorption. The step-flow growth of the dimer rows seem to be proceeded by C_2 under the influence of a pulsed charge (-2 and 0) biased to the single-layer stepped (001) surface.

Keywords: Model calculation, diamond film, step-flow growth, single-layer step, semiempirical molecular orbital method, dimer row, pulsed charge.

1. INTRODUCTION

The growth of diamond films by chemical vapor deposition (CVD) has important role for their potential application in electronic and optical devices. High-quality diamond films with atomically flat surface and low defect density are further required for the electronic device applications. Diamond homoepitaxial films on (001) substrates exhibited better quality than those on (110) and (111) substrates [1-3].

Tsuno *et al.* studied with scanning tunneling microscopy (STM) and reflection high-energy electron diffraction (RHEED) observations of homoepitaxial diamond layer grown on the diamond (001) surfaces by microwave plasma CVD (MPCVD) using $CH_4(6\%)/H_2$ at $830^\circ C$ [4]. The RHEED pattern exhibited 2×1 and 1×2 dimer structures along the (110) direction. The images of the atomic level corresponding to the RHEED pattern were obtained by STM. The direction of the dimer rows in an area was perpendicular to those in other area, which was lower than the former area by 0.9 \AA of a monatomic step. The homoepitaxial growth of the (001) diamond films has mainly been performed in a step-flow growth mode [4-6]. The more detailed STM images of (001) 2×1 dimer rows gave the homoepitaxial diamond (001) layer grown using $CO(5\%)/H_2$ by Kawarada *et al.* [7]. Tsuno *et al.* proposed the following models for the growth on diamond (001) substrates [8]. First, the growth with $CH_4(2\%)/H_2$ depended on the step flow in the small rate of two-dimension nucleation. Second, the rate of two-dimensional nucleation increased with the increase of methane concentration, $CH_4(6\%)/H_2$. The step-flow growth

process has not yet been determined clearly. Theoretical studies are required for developing perfect crystal quality.

By the model calculation of semi empirical molecular orbital methods, Yanagihara asserted that CH and CH_2 adsorbed on a vacant H site of the hydrogenated diamond (111) surface exerted positive influence on homoepitaxial growth by the application of a pulsed negative charge (-1) or an alternating charge (-1 and $+1$) bias to the substrate [9]. The adsorptions of CH and CH_2 onto the diamond (111) surface had determined by using the nucleation theory. The experimental studies suggested that the charges required for the growth were given by plasma [10]. Mehandru and Anderson further obtained stable monolayer CH_2 chemisorption and observed that the CH_2 easily picked up a H gas to form a CH_3 during the diamond growth process [11]. Yanagihara furthermore suggested that CH and CH_2 adsorbed on the $\{111\}$ B surfaces of c-BN exerted positive influence on the nucleation by positive charge biased [12]. The abstractions of the surface H atom on the $\{111\}$ N surfaces are however impeded because frontier orbitals of the surface H atom interacted less effectively with frontier orbitals of the H gases. Based on their results, they suggested that nucleation on the $\{111\}$ N surfaces did not proceed. The results corresponded to ones of the heteroepitaxial diamond growth on the $\{111\}$ surfaces of c-BN using d.c. plasma CVD by Koizumi and Inuzuka [13]. That is, the boron-terminated $\{111\}$ B surfaces were all covered with diamond film, while such deposition hardly occurred on nitrogen-terminated $\{111\}$ N surfaces.

For diamond films growth on the (001) 2×1 surface, Garrison *et al.* [14] had suggested that CH_2 radicals were highly reactive and important for growth. But, our calculated results have deduced that dimers, C_2 , are important for the step-flow growth of diamond (001) surface by using nucleation theory and a frontier orbital theory [9, 12].

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2. CALCULATING METHODS

The PM5 approximation of MOPAC 2002 for semiempirical molecular orbital calculations was used for solving the Schrödinger equation at the Hartree-Fock level in the quantum chemical optimization of atomic cluster geometry [9, 15, 16]. In modeling the crystal structure, this approximation is appropriate for the calculations of geometric optimization of large clusters formed with numerous atoms in a short time.

Fig. (1) shows a model of a diamond cluster M_1 , $C_{173}H_{104}$, with a stepped hydrogenated (001) face bound by four $\{111\}$ faces. The large gray and small black balls respectively represent carbon and hydrogen atoms. The H monohydride phase has been assumed except for the edge sites $\{111\}$ and vacant hydrogen atom sites. The starting species M_1 has been used in the growth mechanism. The calculations can be used to discuss only the reactions over the barrier of activation energy at 1200 K.

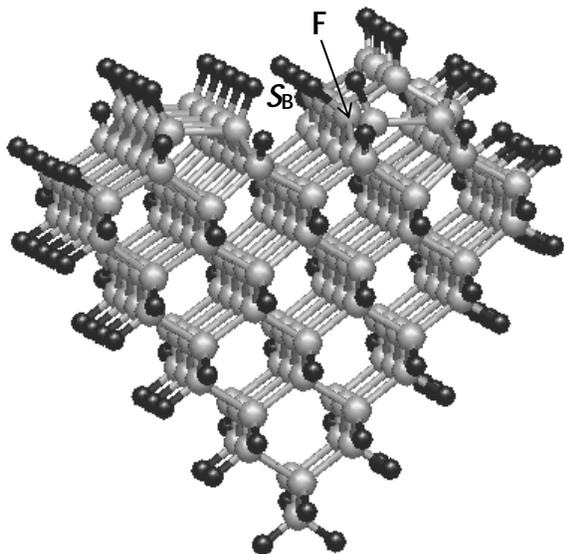


Fig. (1). Model of diamond cluster M_1 , $C_{173}H_{104}$, with a stepped hydrogenated (001) face bound by four $\{111\}$ faces.

Regarding diamond growth by CVD in a CH_4/H_2 gas mixture, both the abstractions of the surface H atoms and the chemisorption by a radical gas on the substrate are important. In the present study, the growth for the chemisorption is slowly in comparison with the one by Van der Waals' forces [9, 17]. First, the pair of surface H atoms is abstracted by 2H gases and the pair vacant H atom sites are produced. Next, radical gases bond onto the vacant H atom sites. The relative stability of the cluster structures in these models has been estimated on the basis of the heat of formation (HOF) obtained by PM5 calculations.

A chemical interaction between the gas and the cluster surface during diamond growth by CVD has been analyzed based on the electronic energy levels of the interacting fragments of cluster and gas molecules [9, 18]. The

interactions between the two systems are pair wise additive over the molecular orbital each pair interaction as follows:

$$\Delta E = |H_{ij}|^2 / (E_i - E_j), \quad (1)$$

where H_{ij} is proportional to the overlap integral and the eigenvectors (coefficients) of the atomic orbitals in the molecular orbitals, i and j , for the interaction. $(E_i - E_j)$ denotes the difference in energy of the molecular orbitals i and j .

Assuming the quasi-equilibrium, the formation probabilities of the products from the reactants at temperature T are obtained as follows. The existence of gases k and l of number density n_k and n_l is assumed on the surface of a cluster. Giving the formation probabilities of the clusters K and L for the gases k and l on the surface of a cluster M by P_K and P_L ,

$$P_L / P_K = n_l / n_k \cdot \exp[(G_K - G_L) / kT], \quad (2)$$

where, G_K and G_L are the binding energies of the gases k and l bonded with the cluster M , respectively. The surface diffusion energies of the radical gases are excluded in Eq. (2) because these are very small compared with the binding energies.

The binding energy G_K is given by

$$G_K = \Delta H_f(K) - [\Delta H_f(M) + \Delta H_f(k)], \quad (3)$$

where, $\Delta H_f(K)$ and $\Delta H_f(M)$ represent the HOFs in the clusters K and M , respectively. As the HOF, $\Delta H_f(k)$, for gas k , we have used the standard HOFs for gases [9].

3. STEP-FLOW GROWTH OF DIAMOND ON STEPPED DIAMOND (001) SURFACE

a) Growth of Diamond on the Single-Layer S_B of "Nonbonded" Edge

A diamond cluster model M_1 , $C_{173}H_{104}$, with the stepped hydrogenated (001) face bound by four hydrogenated $\{111\}$ faces is shown in Fig. (1). Atom marked (F) is the carbon atom at the kink site. The (001) surface is composed by the two single-layer S_A and S_B steps, as shown in Fig. (2a). Large shaded and gray circles represent carbon atoms on the upper-terrace and lower-terrace, respectively. The subscripts, A and B, respectively denote as normal and parallel to the step edge for the dimerization direction of the carbon atoms on an upper terrace near a step [19]. The S_B step has also simple "nonbonded" edge geometry. The S_A and S_B steps compose a kink site (F) at these boundaries. The model has been used as the starting species in the growth mechanism.

The relative energies for HOFs of four clusters are shown as a function of the charges biased to the clusters in Table 1. P_1 , $C_{173}H_{102}$, has a pair of vacant H atom sites on two carbon sites (F) and (G) along the stepped edge of S_B , as shown in Fig. (2a). P_1 , C_2 and P_1 , C_2H_2 are the clusters with C_2 , and C_2H_2 bonded onto the pair of vacant H atom sites (F) and (G), respectively. The abstraction of the surface H atoms from the neutral surface of the stable $M_1(0)$ is impeded by the high barrier of 462 kJ/mol ($1\text{kJ/mol} = 1.036 \times 10^{-2} \text{eV}$).

The reactions of radical gases and the surface H atoms of the stepped (001) diamond surfaces are given by Eq. (1). The HOF of $M_1(2-)$ of a negative charge -2 biased to the substrate becomes -1105 kJ/mol for the geometric meta-

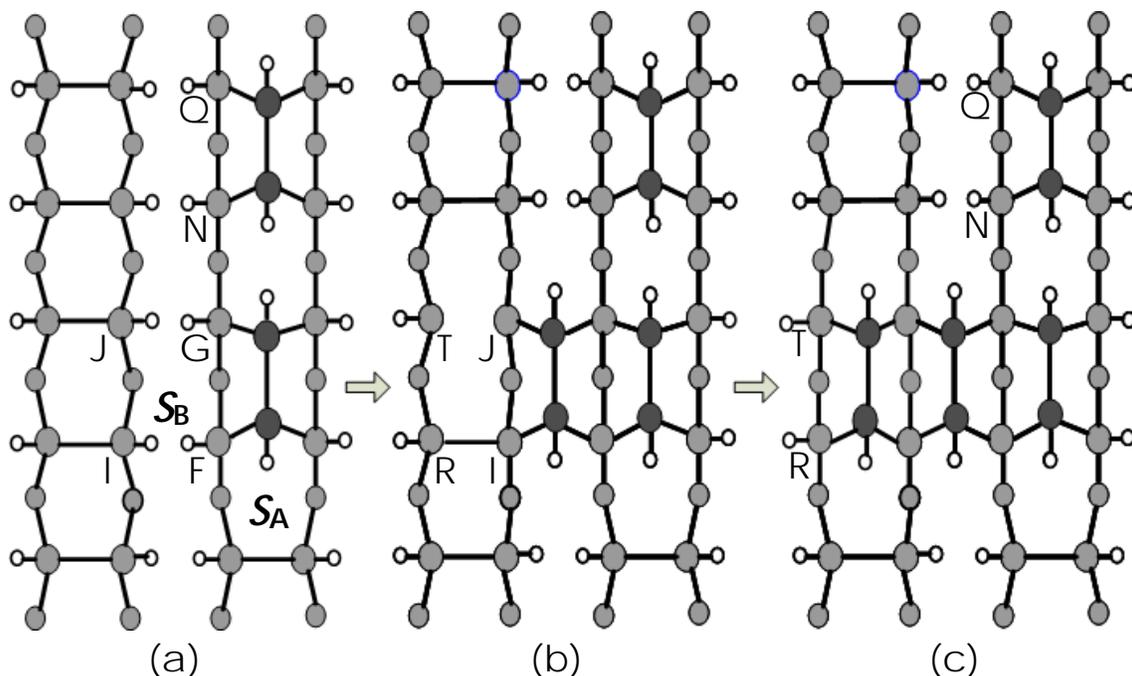


Fig. (2). A top view model for the extension of single dimer row on (001) surface.

stable state. The surface H atoms on the carbon sites (F) and (G) of $M_1(2-)$ in Fig. (2a) are relatively large total electronic densities 0.021 and 0.033 in the high occupier molecular orbitals of -4.39eV and -3.94eV , respectively. The electrons are effectively interacted with the electron energy level, -3.40 eV , at $n=2$ of a gas of H atoms. A pair of surface H atoms is therefore abstracted from the surface by 2H gases and $M_1(2-)$ becomes to the cluster $P_1(2-)$ with a pair of vacant H sites. The binding energy of two surface H atoms on the carbon sites (F) and (G) of $M_1(2-)$ is -240 kJ/mol , as shown in Table 2. Comparing with the binding energy of the surface H atoms on the flat (001) 2×1 surface given a negative charge -2 , -317 kJ/mol , the present binding energy is considerably small. The negative charge given to $M_1(2-)$ distributes widely over the whole structure. In the cluster $P_1(2-)$, the negative charge of -2 compensates the charges of two dangling bonds on the two surface vacant H sites (F) and (G), and the whole structure is stabilized by the abstractions. HOF of $P_1(2-)$ becomes the stable state of -1301 kJ/mol (Table 1).

Table 1. Heat of Formation (HOF) Calculated as a Function of the Charges for Clusters

Cluster	Energy for HOF (kJ/mol)			
	Charge Given to Cluster			
	0	-2	-4	2
$M_1(\text{C}_{173}\text{H}_{104})$	-1742	-1105	256	-42
$P_1(\text{C}_{173}\text{H}_{102})$	-1280	-1301	43	-20
$P_1\cdot\text{C}_2$	-958	-933	377	699
$P_1\cdot\text{C}_2\text{H}_2$	-1461	-1042	—	193

Table 2. Binding Energy Calculated by Eq. (3) for 2H , C_2 , and C_2H_2 on the Cluster P_1

Gas	Binding Energy ϵ_k (kJ/mol)			
	Charge given to cluster			
	0	-2	-4	2
2H	-898	-240	-223	-458
C_2	-516	-470	-504	-119
C_2H_2	-408	32	—	-14

When 2H gases by an exothermic reaction remove a pair of surface H atoms from two carbon sites of the cluster $M_1(2-)$, the heats of reaction, ΔH , for the abstraction of the pair of surface H atoms at 298K are calculated as a function of charge. The cluster $P_1(2-)$ with a pair vacant H atoms on the sites (F) and (G) are produced; $M_1(2-) + 2\text{H} = P_1(2-) + 2\text{H}_2$ ($\Delta H = -632\text{ kJ/mol}$). Also, the heats of reaction for C_2 in the abstraction of two surface H atoms show the great value of -807 kJ/mol . When the step-flow growth is dominant in the growth with $\text{CH}_4(2\%)/\text{H}_2$, the concentration of C_2 is the smaller quantity than 2% [4]. As the concentration is proportional to the reaction rate, the reaction rate of 2H is very higher than C_2 . 2H radical gases are therefore supposed the larger contribution than C_2 for the abstraction of a pair surface H atoms from $M_1(2-)$.

In $M_1(4-)$ given negative charge of -4 , a pair of surface H atoms on the carbon sites (F) and (G) is abstracted by 2H gases. $M_1(4-)$ is transformed to $P_1(4-)$. The binding energy of the surface H atoms is the small value of -223kJ/mol . As the binding energy of the surface H atoms on the carbon sites

(N) and (Q) of $P_1(4-)$ increases to -408kJ/mol, the surface H atoms are not abstracted by 2H gases. The dangling orbits of the vacant sites (F) and (G) of $P_1(2-)$ have the very large total electron densities 1.44 and 1.44 at the highest occupier molecular orbital (HOMO) of 0.51eV, respectively. The orbits interact effectively with the lowest unoccupied molecular orbital (LUMO) -0.04eV of C atomic gas by Eq.(1). The kink site (F) has also the highest surface diffusion density of C gases and the highest reaction rate. In this model calculation, 2C gases on the sites (F) and (G) change instantaneously to C_2 by the large binding energy of -598kJ/mol and become to the cluster $P_1(2-)\cdot C_2$. The HOF of $P_1(2-)\cdot C_2$ is -933kJ/mol at the meta-stable state, as shown in Table 1. The binding energy between the C_2 and $P_1(2-)$ gets -470kJ/mol by Eq. (3) using HOF of C_2 , 838kJ/mol [9]. The C_2 on $P_1(2-)$ changes to C_2H_2 by the abstraction of the two surface H atoms from the carbon sites (I) and (J) on the lower terrace and $P_1(2-)\cdot C_2$ becomes to $P_1'(2-)\cdot C_2H_2$. The negative charge -2 biased to the substrate is localized at the four carbons, (F), (G), (I), and (J), and these carbons repel each other. The C_2H_2 on the neutral surface of $P_1'(0)\cdot C_2H_2$ forms a bridge bonded on the two vacant H atom sites of (I) and (J) and the cluster is shown as $M_2(0)$ in Fig. (2b). In the case of 2CH on $P_1(2-)$, 2CH gases become instantaneously to C_2H_2 by the binding energy -961kJ/mol. But, C_2H_2 can not bond onto these sites by small repulsion power of 32kJ/mol.

When ϵ_K and ϵ_L are respectively the binding energies of 2H and C_2 bonded onto the $P_1(2-)$, the values of formation probabilities in the Eq. (2) at 1200 K have been calculated using the values of ϵ_K and ϵ_L . The exponential factor in the ratios of the formation probabilities between 2H and C_2 is 1×10^{10} . The values of n_1 / n_k becomes smaller than 10^{-2} when n_k and n_1 are the number densities of 2H and C_2 , respectively. The formation probability of C_2 bonded onto $P_1(2-)$ is however greater than the others. These rough approximations are sufficient for determining of radicals for the contribution to the nucleation.

b) Growth on the Single-Layer S_B Step of “Rebonded” Edge

The cluster M_2 , $C_{175}H_{102}$, with the single-layer S_B step of two “rebonded” edges, (I) and (J), grown from M_1 is shown in Fig. (2b). In the calculation of the geometric optimization, the bond on the carbon sites (J) and (T) is broken by a negative charge -2 biased to the substrate, and $M_2(2-)$ becomes to the meta-stable state at the HOF, -971 kJ/mol. The two carbons of (J) and (T) have the large electron densities of 0.235 and 0.508 at the HOMO of 1.12 eV, respectively. The two carbons of (I) and (R) respectively are also relatively large electron densities of 0.079 and 0.062 at the high occupier molecular orbital of -3.13 eV. C_2 formed by binding of 2C on the sites, (J) and (T), makes a bridge onto the carbon sites, (J), (T), (I), and (R). C_2 onto the $M_2(2-)$ has a large binding energy of -875kJ/mol. The bridge, C_2 , on the neutral surface $M_2(0)$ picks up 2H gases by the binding energy of -814kJ/mol, and C_2 changes into C_2H_2 , as shown in Fig. (2c). $M_2(0)\cdot C_2H_2$ of the neutral charge becomes the stable state. A single dimer row is proceeded by C_2 under the influence of a pulsed charge (-2 and 0) biased to the stepped surfaces.

The experimental studies of diamond growth suggest that the charges are supplied by plasma. It is guessed that the pulsed charge necessary for growth is given when the plasma changes from the minus charge into the plus charge.

In the calculation of the geometric optimization, $M_2(0)$ and $M_2(2+)$ do not break the bond. In $M_2(2+)$, the positive charge +2 biased to the substrate is localized on the surface hydrogen atoms. Here, $M_2\cdot C_2H_2$ with the double-layer D_B step is remade to M_3 .

c) Growth on the Double-Layer D_B Step of “Nonbonded” Edge

The cluster M_3 , $C_{183}H_{110}$, with double-layer D_B step of the dimerization direction on an upper terrace parallel to the step edge, is shown in Fig. (3). Atom marked (R) is the carbon atom at the kink site of D_B and S_A steps. Fig. (4) shows the cluster $P_3\cdot C_2$ with the dimer C_2 , (U) and (V), bonded on the double-layer D_B step of cluster P_3 , $C_{183}H_{108}$. The circles of large shadow and gray represent carbon atoms of dimer rows on the upper-terrace and lower-terrace, respectively. The total electronic densities of two surface H atoms on the carbon sites of (R) and (T) are relatively large 0.018 and 0.027 in the high occupier molecular orbitals of -4.10eV and -3.50eV, respectively. In $M_3(2-)$, a pair of surface H atoms on the sites (R) and (T) has the binding energy of -237kJ/mol. If a pair of surface H atoms on the sites (R) and (T) is abstracted by 2H gases, $M_3(2-)$ is transformed to $P_3(2-)$ with a pair of vacant surface H atoms on the carbon sites (R) and (T). The heat of reaction of the abstraction of two surface H atoms is 628kJ/mol. In $P_3(2-)$, the given negative charge is localized on the dangling bonds of carbon sites (R) and (T). The total electron densities of (R) and (T) are also respectively very large 0.618 and 0.930 at HOMO, 0.44eV. C_2 formed by 2C gases on the sites (R) and (T) is bonded onto the $P_3(2-)$, $C_{183}H_{108}$, by the binding energies of -473kJ/mol. The sites (U) and (V) of C_2 in Fig. (4) are large negative charges of -0.62 and -0.53, respectively. Two surface H atoms on the sites (W) and (X) of the lower terrace are positive charges 0.26 and 0.34 of about three times or more than the circumferential ‘surface’ H atoms, respectively. The coulomb interactions are therefore obviously among these four atoms. The C_2 however cannot abstract the surface 2H atoms on the sites (W) and (X). The average of the distances between the H atoms and the carbons, (U) and (V), of C_2 respectively is about 0.23nm and it is longer than about 0.19nm of $P_1\cdot C_2$. The C_2 on the neutral surface easily picks up 4H gases with the large binding energy of -1519kJ/mol and C_2 becomes to C_2H_4 . The C_2H_4 on $P_3(2-)\cdot C_2H_4$ given a negative charge -2 is evaporated from the substrate by large repulsion power, 251kJ/mol. Two vacant surface H sites (R) and (T) on the neutral surface of $P_3(0)$ capture the 2H gases and comes back to $M_3(0)$ of Fig. (3). The growth of the dimer row from $P_1(2-)\cdot C_2$ therefore stops at this stage. The growth of next dimer row then restarts from the carbon sites (N) and (Q) of two vacant surface H atoms.

On the other hand, the binding energy of the surface H atoms on the sites (N) and (Q) is -245kJ/mol. If the surface H atoms are abstracted by H gases, $M_3(2-)$ is transformed to $P_3'(2-)$. Two vacant surface H atom sites (N) and (Q)

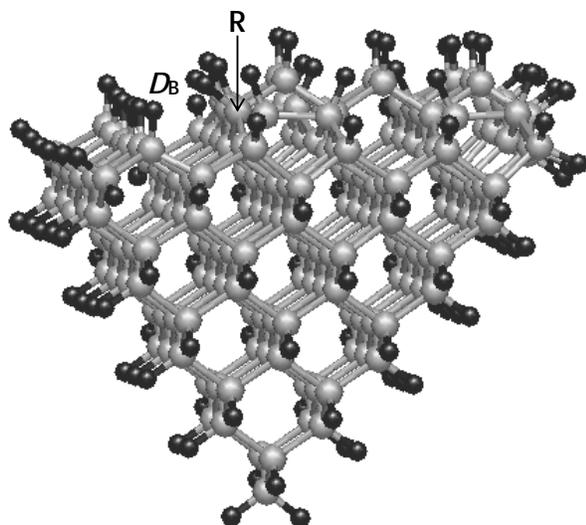


Fig. (3). Model of diamond cluster M_3 , $C_{183}H_{110}$, with a double-layer D_B stepped hydrogenated (001) face bound by four $\{111\}$ faces.

respectively are very large total electron densities 0.618 and 0.930 in the HOMO of 0.439eV. C_2 formed by 2C gases onto (N) and (Q) is bonded onto the $P_3'(2-)$ by the binding energy of -481kJ/mol. The dimer rows from $P_3'(2-)\cdot C_2$ grow in the same way similar to the previous studies.

4. CONCLUSIONS

Step-flow growths of diamond on the single-layer steps of “nonbonded” edge and “rebounded” edge in the hydrogenated diamond (001) surface have been investigated using the semiempirical molecular orbital method PM5. The chemical reactions at the first stage of growth have been calculated as a function of the charges biased to the substrates. The hydrogenated diamond, $M_1(2-)$, of a negative charge -2 biased becomes unstable. The surface H atoms are abstracted by 2H gases, $P_1(2-)$. C_2 formed by 2C atomic gases is bonded onto the vacant H atom sites, $P_1(2-)\cdot C_2$. The C_2 on the cluster changes to C_2H_2 by the abstraction of two surface H atoms on the lower terrace, $P_1'(0)\cdot C_2H_2$. The C_2H_2 on the neutral surface of $P_1'(0)\cdot C_2H_2$ forms a bridge bonded with the two vacant H atom sites on the lower terrace and it becomes to $M_2(0)$, as shown in Fig.(2b).

The cluster M_2 with the single-layer S_B step of “rebounded” edge becomes unstable by the negative charges. The “rebounded” edge of (J) and (T) is broken by the charge -2 biased to the substrate. C_2 formed by 2C gases on the broken bond sites makes the bridge bonded on the four carbon sites and $M_2(2-)$ becomes $M_2(2-)\cdot C_2$. The C_2 on the neutral surface picks up 2H gases and it changes to C_2H_2 . $M_2(0)\cdot C_2$ becomes $M_2(0)\cdot C_2H_2$ of stable state, as shown in Fig. (2c). When $M_2\cdot C_2H_2$ meets to a double-layer D_B step, M_3 of Fig. (3) is remade.

When a pair surface H atoms on the carbon sites (R) and (T) of $M_3(2-)$ is abstracted by 2H gases, C_2 bonds on the vacant H atom sites and $M_3(2-)$ become to $P_3(2-)\cdot C_2$ in Fig. (4). The C_2 on $P_3(2-)\cdot C_2$ can not abstract the two surface H atoms of the lower terrace. The C_2 on the neutral surface picks up 4H gases and C_2 changes to C_2H_4 . The C_2H_4 on

$P_3(2-)\cdot C_2H_4$ given a negative charge of -2 is evaporated by large repulsion power. The two vacant surface H sites, (R) and (T), on the neutral surface of $P_3(0)$ capture 2H gases and $P_3(0)$ returns to $M_3(0)$. The growth of the dimer row from $P_1(2-)\cdot C_2$ therefore stops here.

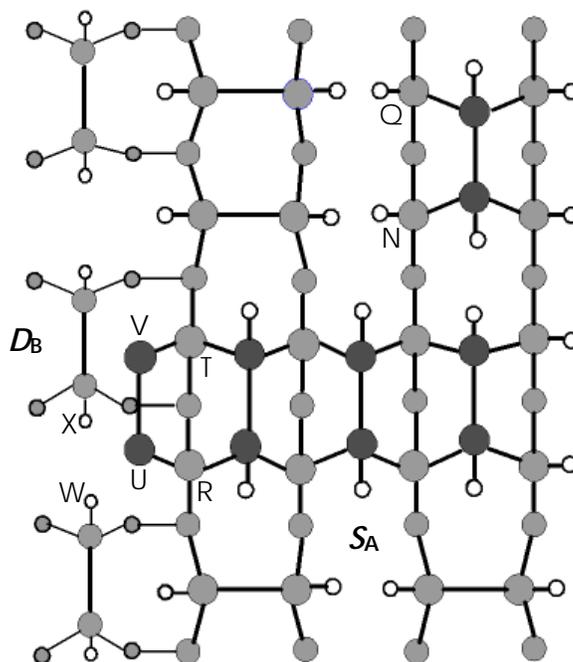


Fig. (4). A top view model of cluster $P_3\cdot C_2$ with the dimer C_2 , (U) and (V), bonded on the double-layer D_B step of cluster P_3 , $C_{183}H_{108}$.

If a pair surface H atoms on the sites (N) and (Q) in Fig. (4) is abstracted by 2H gases, $M_3(2-)$ is transformed to $P_3'(2-)$ with a vacant surface H sites. C_2 bonds on the vacant H atom sites and the dimer row grow in the same way as M_1 . We have therefore deduced that the step-flow growth of the dimer rows is proceeded by C_2 under the influence of a pulsed charge (-2 and 0) biased to the stepped surfaces.

The calculation has excluded the single-layer S_A step for the dimerization direction on the upper terrace to be normal to the step edge, as shown in Fig. (2a). The binding energy of a pair surface H atoms on the lower terrace for -2 has the value of -306kJ/mol greater than -240kJ/mol of $M_1(2-)$.

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