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공학박사 학위논문

# Catalytic effects in diamond growth: An ab-initio study 

다이아몬드 성장에서 촉매 효과들에 대한 제일원리 계산 연구

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# Catalytic effects in diamond growth: An ab-initio study 

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## Abstract

The diamond synthesis began in the 1950s when General Electric of the United States succeeded in the High-Pressure and HighTemperature (HPHT) method. In this process, catalytic metals such as $\mathrm{Fe}, \mathrm{Co}$, and Ni are necessarily required for rapid transformation from graphite to diamond. The main role of catalytic metals has been known to date as the role of a solvent that dissolves carbon sources. Thus, the carbon solubility and melting temperature of the catalytic metal have been chosen as the main parameters to select effective catalytic metals. However, the various experimental results, which cannot be explained by these two parameters of carbon solubilities and melting temperatures, need us to search for an additional parameter for understanding the catalytic effect. In this study, using ab-initio density function theory (DFT), we investigated the microscopic mechanism of the catalytic metals, especially on the diamond surface, and suggest a new parameter concerning the surface catalytic effect.

On the other hand, in the 1970s and 1980s, by developing chemical vapor deposition (CVD) methods using a gas-activation system, such as plasma or hot-filament, diamond synthesis in the form of thin films in a vacuum chamber has been possible, and used for various industrial surface treatments. In this process, a lot of excess charges are produced by the gas-activation, and many experimental results observed that excess charges promoted
diamond formation. However, a proper microscopic mechanism of this excess charge effect has not been elucidated. Therefore, we also investigated the excess charge effect in the diamond growth with a possibility of catalysis of the excess charge on the diamond surface.

Firstly, to understand the physical and chemical roles of catalytic metal Ni in the growth of diamond, ab-initio calculations of the structural, electronic, and kinetic properties of a Ni - covered C (111) surface were performed. Findings from this theoretical study highlight two important roles of Ni in addition to its carbon-solvency effect that is widely known to play a catalytic role in the growth of diamond. The first role is to facilitate the formation of $a$ thermodynamically stable $\mathrm{Ni}-\mathrm{C}$ interface with a diamond bulk-like structure and the second is to induce surfactant-mediated growth enabling continuous layer-by-layer growth for diamond. This presents a new perspective on the surface action of catalytic metal Ni, which has not been previously proposed.

Secondly, the phonon densities of states (ph-DOSs) of clean and Ni-terminated $C(111)$ surfaces with $1 \times 1$ and $2 \times 1$ surface structures were investigated using ab-initio density functional perturbation theory (DFPT). The ph-DOSs showed vibrational spectra associated with the surface structures of $C(111)$ and $\mathrm{Ni} / \mathrm{C}$ (111) represented in the previous chapter. Further analyses of various surface phonon modes were performed to identify vibrational features involving the surface atoms of C (111) and $\mathrm{Ni} / \mathrm{C}(111)$. These features provide important information for experimentally verifying the formation of a diamond bulk-like structure at $\mathrm{Ni} / \mathrm{C}$ (111) and their
catalytic effect on the diamond surface.
Thirdly, based on the previous research results on $\mathrm{Ni} / \mathrm{C}(111)$ system, we examined the effectiveness of all transition metals in the periodic table on diamond $C$ (111) surface. We found that elements in the center region of the periodic table (groups $4,5,6,7,8,9$, and 10) favor the $1 \times 1$ diamond bulk-like interfacial structure, while elements in the edge regions (groups 3, 11, and 12) favor the $2 \times 1$ Pandey chain interfacial structure. It is due to the differences of position, occupation, and bandwidth of d-bands of each transition metal so that the interaction between each metal layer and diamond C(111) significantly differs. The more stable the $1 \times 1$ structure is, the more advantageous diamond growth is by removing the $s p^{2} \pi-$ bonds on the $2 \times 1$ surface and reducing the surface energy of the diamond bulk-like $1 \times 1$ surface. The elements having moderate $\mathrm{M}-$ C cleavage energy would be a good catalytic candidate because it causes moderate $1 \times 1$ stability and moderate growth kinetic barrier for continuous diamond growth in the $\mathrm{M} / \mathrm{C}(111)$ system. We also found that the early transition metals (groups $3,4,5$, and 6 ) are likely to form carbide than to form the $M$ layer on the $C(111)$ surface, which is associated with the low efficiency of early transition metals for a catalyst of diamond growth. In addition to the solubility and melting temperature of metals, interfacial energy representing the surface catalytic effect will be important information to understand the catalytic effect of the transition metals and to design the future catalytic candidates in diamond growth.

Lastly, an ab-initio calculation study is performed on the effect
of excess charges in the CVD diamond growth system. In this way, the differences and limitations of the plane wave (PW) method and the atomic orbital (AO) method under periodic boundary condition (PBC) are investigated. As a result, in the PW method, as the vacuum size was increased, excess electrons spilled out into the vacuum, resulting in severe artifacts. However, in the AO method, this problem did not occur due to the locality of the atomic orbitals. In cells with large vacuum spacing, most of the charge goes to the surface, so the influence of excess charges on $\mathrm{C} 2-\mathrm{C} 3$ bond length in the $1 \times 1$ model structure is insignificant. On the other hand, in the cell with small vacuum spacing, the charge was forcibly entered into the subsurface region due to electrostatic repulsion from the same charges in the external neighboring image cells. As a result, the length of the $\mathrm{C} 2-\mathrm{C} 3$ bond changed significantly. We observed that the length of the $\mathrm{C} 2-\mathrm{C} 3$ bond is shortened as the negative charge increases, which would be related to the stabilization of the $s p^{3}$ diamond bulk-like surface structure by negative charging on the diamond surface. However, the analysis of the charge effect in a low vacuum system requires a more sophisticated theoretical study.

Keyword: Catalytic effect, Transition metal, Diamond surface, Excess charge, Ab-initio calculation, Electronic structure, Phonon spectra, Surfactant-mediated growth

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## Chapter 1. Introduction

### 1.1. Diamond. Its Properties and Applications

Diamond is one of the solid phases made of the element carbon with a unique crystal structure called diamond cubic. It has 8 atoms in its unit cell [see Fig. 1.1], where one atom in the corner is shared by eight neighbor cells, three atoms in the center of a face are shared by two neighbor cells, and four atoms are in the inner cell. The diamond cubic cell can also be imagined as two Face - centered cubic (FCC) cells overlapping $1 / 4$ of the diagonal length apart in the diagonal direction, or two atoms lying at on lattice point. From the <111> crystallographic direction, this has an $A B C A B C . .$. stacking pattern of repeated layers. Each atom in the diamond cubic has four $S p^{3}$ hybrid bonds with four neighboring atoms, forming a local tetrahedron structure with a bond angle of $109.5^{\circ}$ and a bond length of $1.54 \AA$. This tetrahedron structure is the reason for the high density and strength of the diamond [1].

Because of its very high hardness and thermal conductivity, diamond is used as a surface treatment for cutting tools [2] or as a heat dissipating material [3], and due to low adhesion and friction, it is used as an abrasive for various metals [4]. It shows excellent optical and electrical resistance in pure diamond, and when it is doped, it shows high power $[5,6]$ and carrier mobility $[7,8]$, showing
potential as a next-generation electronic material. Recently, diamond involving nitrogen-vacancy (NV) is in the spotlight in quantum computing, quantum communication, and quantum sensors [9-12]. Diamond can also be used as a biomedical material because of its chemical inertness and biological compatibility [13-15].

Another solid phase made of carbon is graphite, which is a more stable structure than diamond at room temperature and pressure. The graphite phase forms a plane structure called graphene at an angle of $120^{\circ}$ and a bond length of $1.42 \AA$ through $s p^{2}$ hybrid bonds with three neighboring atoms, and the planes are connected by Van der Waals force. The bonds within the plane are stronger than bonds in the diamond, but the bond between planes is very weak in graphite [1].

The pressure and temperature equilibrium lines between graphite and diamond are well established from experimental and theoretical results [16]. The equilibrium line increases linearly from 1.7 GPa and 0 K to 12 GPa and 5000 K , the triple point of graphite, diamond, and liquid. The carbon solid polymorphs exist well in a metastable state once it is formed because of its high cohesive and activation energy. For example, metastable diamond exists well at room temperature where graphite is the stable phase. Also, in order to transform graphite to the diamond even in the diamond stable region, a much higher temperature and pressure than the equilibrium line must be applied.


Figure 1.1 Conventional cubic unit cell of diamond containing eight atoms. Image generated using VESTA.

### 1.2. Diamond Synthesis

Synthetic diamonds are diamonds made by 'human hands' in a laboratory, as opposed to those made in nature and obtained from mines. These synthetic diamonds are nothing different from natural diamonds at the molecular level [17, 18]. In recent years, it has become possible to make large synthetic diamonds of gem-quality [19, 20]. Jewelry and numerous industrial applications still demand a lot of synthetic diamonds. Since the first successful production of synthetic diamonds in the 1950s, numerous methods of making synthetic diamonds have been developed over half a century.

The first synthetic diamond manufacturing method, developed in the 1950s by Generic Electric company, is a High-Pressure and High-Temperature (HPHT) method [21] that simulates the environment inside the earth. This method, along with the explosive method, is currently the most widely used commercially. In this method, a catalytic metal is necessarily required, and mainly known catalytic metals are $\mathrm{Fe}, \mathrm{Co}$, and Ni [22]. The role of the catalytic metal known to date is that it first melts at its metal-carbon eutectic temperature to become a liquid phase, and serves as a solvent to dissolve carbon sources such as graphite or micro diamond particles. However, the results that have not yet been interpreted only using carbon solubility and melting temperature indicate that further research is needed on the catalytic mechanism of these metals for diamond synthesis [23-26].

Another well-known synthetic diamond growth method is chemical vapor deposition (CVD), which occurs at very low pressures below atmospheric pressure. In this method, precursors such as methane diluted with hydrogen (typically $1-5 \%$ methane) are fed into a low-pressure vacuum chamber, and they are decomposed by a gas-activation system and deposited in the form of thin films on the substrate. Most of the CVD methods is using gas activation through plasma from a microwave or induced capacitance device, or thermal electron and photon emission from hot-filament built in the chamber [27,28]. What is known about the role of gasactivation to date is that it decomposes precursor molecules. In addition to this, Hwang et al. suggested a new perspective on the role of excess charges from the gas-activation system and their charging effect on diamond particles nucleated in a vacuum chamber [29-34].

### 1.3. Diamond (111) Surface

As a starting system for calculation, the $C$ (111) surface, which has the lowest surface energy among diamond surfaces, is an important and basic plane. Its surface structure plays an important role in determining the morphology of the growing diamond and many other physical properties [35-37]. As for the clean C(111) surface, the $2 \times 1$ reconstruction was observed. Although the detailed atomic geometry of the reconstructed surface is still controversial, most experimental and theoretical studies [38, 39] support the Pandey
$\pi$-bonded chain model. The $s p^{2} \pi$-bonded chain structure of the $2 \times 1$ reconstructed surface would prevent the surface $C$ atoms from forming $s p^{3}$ bonds on the diamond surface. Thus, this $\pi$-bonded $2 \times 1$ reconstruction would require the energy for the deformation of the surface $\pi$-bonds and it is more favorable to the growth of graphite than to that of the diamond.

Although a liquid-solid interface should be used to understand the growth of diamond in metal catalyst solvent system at HPHT, such an approach with the liquid-solid interface is not effective to give systematic information to the catalytic effect of metal elements in the growth of diamond in M and $\mathrm{C}(111)$ systems [M/C(111)] because the liquid-solid interface exhibits many complex atomic structures. To avoid this obstacle, we use a solid-solid M/C(111) interface model with a periodic arrangement of M atoms. Generally, solid-solid interface structures have stronger interactions between the M and the C substrate than the liquid-solid interface structures, for the coordination number of solid M with neighboring C substrate atoms is higher than that of liquid M . Thus, it is noted that, if the calculations give unpreferable results for the growth of diamond with the solid-solid interface, the system also is not able to be a good candidate as a catalyst for the growth of diamond in metal catalyst solvent at HPHT. Therefore, this solid-solid interface of M/C (111) could be a good first step in systematically determining the catalytic effect of elements, especially in structural changes between the $\pi$ bonded $2 \times 1$ and the diamond bulk-like $1 \times 1$ interface structures.

## Chapter 2. Theoretical Background

### 2.1. Born-Oppenheimer Approximation

Non-relativistic time-independent Schrödinger equation for a many-body system of interacting nuclei and electrons is as follows

$$
\mathrm{H} \Psi\left(R_{I} ; r_{i}\right)=\mathrm{E} \Psi\left(R_{I} ; r_{i}\right)
$$

where H and E denote the Hamiltonian and total energy of the system and, using atomic units $\hbar=m_{e}=e=1$, Hamiltonian is described as

$$
\begin{aligned}
& \mathrm{H}=-\sum_{I=1}^{N} \frac{1}{2 M_{I}} \nabla_{R_{I}}^{2}-\sum_{i=1}^{n} \frac{1}{2} \nabla_{r_{i}}^{2}-\sum_{i=1}^{n} \sum_{I>i}^{N} \frac{Z_{I}}{\left|r_{i}-R_{I}\right|}+\sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{\left|r_{i}-r_{j}\right|} \\
&+\sum_{l=1}^{N} \sum_{J>I}^{N} \frac{Z_{I} Z_{J}}{\left|R_{I}-R_{J}\right|}
\end{aligned}
$$

Here, $M$ is the mass ratio of nucleus $I$ to an electron and Z is the atomic number of nucleus $I . R$ and r are the positions of the nuclei $I$ and electron $i$. The meaning of each term is, in order, the first and second are the kinetic energy of atoms and electrons respectively, the third is the coulomb interaction between the atom and the electron, and the fourth and the fifth are the Coulomb interaction between the atoms and the electrons, respectively.

In many cases, the mass of an electron is about three or four orders of magnitude lighter than the mass of an atom, so we can think of the electrons as potential with a fixed configuration, where the electrons move instantly. Therefore, separating the motion of the electron from the motion of the atom, we can write the electron Schrödinger equation as

$$
H_{e l} \Psi\left(r_{i}\right)=E_{e l} \Psi\left(r_{i}\right)
$$

with the electronic Hamiltonian $H_{e l}$

$$
H_{e l}=-\sum_{i=1}^{n} \frac{1}{2} \nabla_{r_{i}}^{2}-\sum_{i=1}^{n} \sum_{I>i}^{N} \frac{Z_{I}}{\left|r_{i}-R_{I}\right|}+\sum_{i=1}^{n} \sum_{j>i}^{n} \frac{1}{\left|r_{i}-r_{j}\right|}
$$

The total energy of the system can be obtained by adding the interaction terms between atoms as follows.

$$
E=E_{e l}+\sum_{l=1}^{N} \sum_{J>l}^{N} \frac{Z_{I} Z_{J}}{\left|R_{I}-R_{J}\right|}
$$

This is the Born-Oppenheimer approximation. The calculated total energy gives us a point on the potential energy surface corresponding to a specific atomic configuration and we can find the minimum point of the potential energy surface using various optimization algorithms.

### 2.2. Density Functional Theory

The basic idea of density functional theory (DFT) is the reformulation of a many-body problem that depends on a multivariable set of $\left\langle r_{i}\right\rangle$ into a total density problem that depends on one independent variable r. Kohn and Sham have proposed two theorems on this [40]. The first theorem implies that when electrons are placed under an external potential, the total density of electrons has a one-to-one correspondence with the external potential. Thus, all the characteristics of the system including potential can be obtained through this total electron density, and the total electronic energy can be reformulated as a functional of the total electron density function as follows

$$
\mathrm{E}[\mathrm{n}(\mathrm{r})]=F[n(r)]+\int V_{\text {ext }}(r) n(r) d r
$$

where $F[n(r)]$, the HK functional, represents the sum of the electron kinetic energy $T[n(r)$ ] and the electron-electron potential energy $U[n(r)]$. The second theorem is that, when the electron density function that minimizes functional $\mathrm{E}[\mathrm{n}(\mathrm{r})]$ is obtained through the variational principle, it is the total energy and total electron density of the exact ground state for a given external potential $V_{\text {ext }}(r)$.

However, it is not easy to find the exact functional form of $E[n(r)]$. In 1965, Kohn and Sham [41] showed that the exact ground-state electron density can be expressed in the fictitious system with non-
interacting electrons under an effective potential. Using the noninteracting orthonormal single-particle wavefunctions $\varphi_{i}$, we can write the total electron density as follows

$$
\mathrm{n}(\mathrm{r})=\sum_{\text {occupied }} \varphi_{i}^{*}(r) \varphi_{i}(r)
$$

The electron-electron Coulomb repulsion energy (or Hartree energy) and the kinetic energy of the single-particle wavefunctions is exactly represented by

$$
\begin{gathered}
E_{H}\left[(\mathrm{n}(\mathrm{r})]=\frac{1}{2} \iint \frac{n(r) n\left(r^{\prime}\right)}{\left|r-r^{\prime}\right|} d r d r^{\prime}\right. \\
T_{S}[\mathrm{n}(\mathrm{r})]=\sum_{i}\left\langle\varphi_{i}\right|-\frac{1}{2} \nabla^{2}\left|\varphi_{i}\right\rangle
\end{gathered}
$$

Thus, the HK functional $\mathrm{F}[\mathrm{n}(\mathrm{r})$ ] of real system takes the form

$$
\mathrm{F}[\mathrm{n}(\mathrm{r})]=T_{S}[\mathrm{n}(\mathrm{r})]+E_{H}\left[(\mathrm{n}(\mathrm{r})]+E_{X C}[(\mathrm{n}(\mathrm{r})]\right.
$$

where the exchange-correlation energy, $E_{X C}[(\mathrm{n}(\mathrm{r})]$, contains various correction terms, which are the exchange energy, correlation energy, and the difference between the exact kinetic energy and $T_{S}[(\mathrm{n}(\mathrm{r})]$. These correspond to the difference between a real system and a fictitious system of non-interacting single particles. Now, if we know the functional form of exchange-correlation energy in the Kohn-

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Sham scheme, in principle, we can obtain the total energy from the above equation. In the following section, we will look at the several approximate approaches of the exchange-correlation functional.

### 2.3. Exchange-Correlation Functionals

Many approximate methods have been developed to form the exchange-correlation functional. The simplest way of forming the exchange-correlation energy is the local-density approximation (LDA). In the LDA, it assumes that the exchange-correlation energy at $r, \varepsilon_{X C}[n(r)]$, is equal to that of a homogeneous electron gas with the same electron density $n$. It is described as

$$
E_{X C}^{L D A}[n(r)]=\int n(r) \varepsilon_{X C}^{L D A}[n(r)] d r
$$

One of the famous methods is the fitting to the quantum Monte Carlo calculations for the homogeneous electron gas by Ceperley and Alder.

However, LDA is only effective if it has an almost homogeneous or slowly changing electron distribution. The next level approach is to include gradients or higher derivatives of the charge density. This approach led us to the generalized gradient approximation (GGA). In the GGA, the exchange-correlation functional is described as

$$
E_{X C}^{G G A}[n(r)]=\int n(r) \varepsilon_{X C}^{G G A}[n(r), \nabla n(r)] d r
$$

In many practical cases, GGA outperforms LDA. There are many GGA functionals these days, and the famous one is the PBE functional made by three people Perdew, Burke, and Ernzerhof.

### 2.4. Plane-wave Pseudopotential Methods

### 2.4.1. Plane-wave Methods

The electronic wavefunctions in a periodic system can be expanded by a plane-wave basis set, by the Bloch theorem, as

$$
\varphi_{n, k}(r)=u_{n, k}(r) \exp (i k \cdot r)
$$

with the periodic function $u_{n, k}(r)$ that can be expressed as

$$
u_{n, k}(r)=\sum_{G} C_{n, k}(G) \exp [i(k+G) \cdot k]
$$

Practically, the finite number of plane waves can be used to express the wavefunction. The truncation of the plane-wave basis set can be controlled by introducing a cut-off energy $E_{\text {cut }}$,

$$
\frac{1}{2}|k+G|^{2} \leq E_{\text {cut }}
$$

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Thus, the numerical error in the calculation can be systematically reduced by increasing $E_{\text {cut }}$.

### 2.4.2. Pseudopotential Methods

Describing the electron wavefunctions in the tightly bound core region is hard and cumbersome because it is rapidly oscillating by the orthogonality of electrons, and we need many plane waves to express them. This problem can be overcome by the pseudopotential. The idea behind this is that the core electrons are strongly bound to the nuclei so they rarely participate in the bond formation or chemical reactions. Therefore, in this method, the core electrons are removed and the resulting atomic potential is replaced by a pseudopotential. Thus, valence electrons no longer need to oscillate in the core region, which greatly reduces the number of plane waves to be used. Pseudopotential is generally constructed to match the scattering properties of the actual exact potential. Pseudo wavefunctions are identical to the valence wavefunctions of the real all-electron system beyond the selected core radius and have the same eigenvalues.

# Chapter 3. Beyond-carbon-solvency effects of catalytic metal Ni on diamond growth 

### 3.1. Introduction

The growth of diamonds has attracted a great deal of attention due to its technological importance in a wide range of industrial applications. In 1955, General Electric (GE) succeeded in synthesizing diamonds for the first time [21]. Diamond has been synthesized by use of catalytic metals, such as Fe , Ni, and Co [22]. Until recently, Ni is the main catalyst element under High Pressure and High Temperature (HPHT) method [42-46]. These metals are known to become liquid during the growth processes and carbon exhibits appreciable solubility in these metals. As a result, carbon dissolves in the liquid metal. This process, which is known as the solvent-catalytic effect, is essential to the diamond synthesis.

To understand the effect of indispensable catalytic metals such as Ni on diamond growth, many works have been undertaken. In 1963, Strong at GE investigated the role of the Ni catalyst in the carbonsolvent effect by using copper-rich $\mathrm{Cu}-\mathrm{Ni}$ alloy instead of Ni to reduce the solubility of carbon [23]. Interestingly, the diamond formation was found to be promoted even in the low carbon solubility less than $0.06 \mathrm{at} . \%$ provided by the use of $\mathrm{Cu}-\mathrm{Ni}$ alloys. Furthermore,
increasing the amount of Ni in $\mathrm{Cu}-\mathrm{Ni}$ alloys showed an exponential increase in the number density of nucleated diamond. This behavior is highly contrasted to the results of lead and antimony with their similar low carbon solubility, which showed no diamond formation.

Taking account of these experimental results, this suggests that the carbon-solvency of catalytic metals is a necessary condition but not a sufficient one for the growth of diamond. Based on the nucleation and growth theory, one possible role of Ni in these alloys may be considered as that of reducing the interfacial energy between diamond and alloy. Therefore, the purpose of this chapter is to provide an atomic-scale understanding of the growth processes in the interface between Ni and $\mathrm{C}(111)$ by using ab-initio calculations based on density functional theory (DFT) [40, 41] that can serve as a guide for the design of catalyst systems. We first examine the effect of the Ni overlayer on the $\pi$-bonded chain structure of the $C$ (111) surface, and then, for the continuous growth of diamond, we investigate the kinetic processes for the incorporation of incoming C atoms into the C layer underneath the Ni overlayer, leading to the surfactant-mediated growth of diamond.

### 3.2. Computational Details

All calculations were performed using the spin-unpolarized DFT as implemented in the code of the Vienna $A b$-initio Simulation Package (VASP) [47-49]. The generalized gradient approximation
(GGA) functional of Perdew - Burke-Ernzerhof (PBE) [50] was used to describe the exchange-correlation interactions combined with a projector-augmented wave (PAW) method [51, 52]. The (111) surface of the diamond was simulated by a repeating slab model consisting of 6 atomic C layers (3C bilayers) and a $20 \AA$ vacuum region. The bottom of the slab was passivated by hydrogen atoms, and the lowest carbon layer and hydrogen layer atoms were fixed to simulate the diamond bulk structure. Thereby, the adatom was adsorbed only on one side of the slab. A theoretical equilibrium lattice constant $a_{0}=3.55 \AA$ of bulk diamond was used for the diamond slab. For the structural and electronic properties of the clean and the $\mathrm{Ni}-$ covered $\mathrm{C}(111)$ surfaces, the surface of a $2 \times 1$ rectangular supercell was used in lateral directions (see Fig. 3.1), and the kspace integration was performed using a gamma-centered $6 \times 10 \times 1$ k -point mesh in the Brillouin zone (BZ) of the supercell. For the kinetic processes governing the incorporation of incoming C atoms into the Ni -covered $\mathrm{C}(111)$ [ $\mathrm{Ni} / \mathrm{C}(111)]$ surfaces, a larger $4 \times 2$ surface cell was used to minimize interactions between adjacent incoming C atoms. The electronic wave functions were expanded in plane waves up to an energy cutoff of 400 eV . Geometry optimization was performed until the residual forces acting on the atoms became smaller than $0.02 \mathrm{eV} / \AA$. The spin polarization effect was also tested for both models of $\mathrm{Ni} / \mathrm{C}(111)$. The spin polarization energies, defined as the energy difference between the nonmagnetic and the ferromagnetic states, were less than 0.01 eV . Therefore, spin polarization does not affect the conclusions derived in this study.

Some test calculations were also performed with varying computational parameters such as the energy cutoff, the $\mathbf{k}$-point mesh, and the computational surface unit cell. These tests show that the surface energy difference between the $\pi$-bonded $2 \times 1$ and the diamond bulk-like $1 \times 1 \mathrm{C}(111)$ structures was accurate up to 0.005 $\mathrm{eV} /(1 \times 1$ surface $)$ when using the above computational parameters. As such, the computational accuracy is enough for our study.

For a more detailed analysis of the electronic structures, projected crystal orbital Hamilton population (pCOHP) analysis [53, 54], which is a partitioning scheme of the band-structure energy (Kohn-Sham energy in the plane-wave DFT calculation) in terms of orbital-pair contributions, was employed using the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) package [55]. The energy - resolved pCOHP provides a quantitative measure of bonding, non-bonding, and anti-bonding contributions in the DFT calculations.


Figure 3.1 Top and side views of geometry-optimized atomic structures of the $1 \times 1$ and the $2 \times 1$ models for the clean $\mathrm{C}(111)$ and the Ni -covered $\mathrm{C}(111)$ surfaces with a full monolayer surface coverage of Ni (corresponding to two Ni atoms per the $2 \times 1$ surface unit cell): (a) clean $1 \times 1 \mathrm{C}(111)$, (b) $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, (c) clean $2 \times 1 \mathrm{C}(111)$, and (d) $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$. The $2 \times 1$ surface unit cell used in the calculations is denoted by the black lines. The numbers in the side views of the atomic structures indicate the bond lengths and the bond angles. These values are compared with the bond length ( $1.54 \AA$ ) and the bond angle ( $109.5^{\circ}$ ) of a C atom for bulk diamond. Cn and $\mathrm{Cn}^{\prime}$ denote the C atoms in the n -th C layer.

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### 3.3. Results and Discussion

### 3.3.1. Structures and Energetics

Before we report the physical properties of the Ni -covered diamond $\mathrm{C}(111)$ surfaces, we first summarize our calculation results for the energetics of the clean diamond $\mathrm{C}(111)$ surfaces. Total energy calculations for various models of $\mathrm{C}(111)$ surfaces were performed to determine the relative stability of the $\mathrm{C}(111)$ surface. The two important models among them were: (i) $1 \times 1$ model and (ii) Pandey $\pi$-bonded chain model with the $2 \times 1$ models, respectively, which agree well with the previous calculations [5658]. Among the various models calculated, our results support the $\pi$-bonded $s p^{2}$-like $2 \times 1$ chain model as the most stable surface structure of $\mathrm{C}(111)$. The surface energy of the $2 \times 1$ model was 0.78 $\mathrm{eV} /(1 \times 1$ surface $)$ lower than that of the $1 \times 1$ model. The surface energy difference is in good agreement with previous results [5861].

Next, we investigate the structural stability of the $\mathrm{Ni} / \mathrm{C}(111)$ surfaces. The single Ni atomic layer corresponding to a single monolayer (ML) of surface Ni coverage was adsorbed on C(111) surfaces of the $1 \times 1$ and the $2 \times 1$ models. The (interface) energy of the $\mathrm{Ni} / \mathrm{C}(111)$ with the $2 \times 1$ model is $0.30 \mathrm{eV} /(1 \times 1$ surface $)$ higher than that with the $1 \times 1$ model. This result suggests that the $\mathrm{Ni} / \mathrm{C}$ (111) with the $1 \times 1$ model of interfacial diamond bulk-like ( $s p^{3}$ )

C atoms is the most stable interface structure of $\mathrm{Ni} / \mathrm{C}(111)$, in sharp contrast to the case of the clean $\mathrm{C}(111)$ surface. These energy calculation results are well documented in Table 3.1.

Investigation of the geometry -optimized structures [see Fig. 3.1] shows that, when the Ni atoms are adsorbed on $\mathrm{C}(111)$ of the $1 \times 1$ model, the bond angle and the bond lengths of the C atoms of the top three C layers revert to those of the diamond bulk structure. The bond length between the outermost C atoms changes from $1.48 \AA$ to $1.53 \AA$, close to the bond length of $1.54 \AA$ for bulk diamond. The bond angle of the second layer C atom changes from $100.3^{\circ}$ to $107.7^{\circ}$, close to the bond angle of $109.5^{\circ}$ for bulk diamond. The bond length between the second-and third-layer C atoms changes from $1.70 \AA$ to $1.59 \AA$. This structural change induced by the adsorption of the Ni surface atoms stabilizes the diamond bulk-like structure of $\mathrm{Ni} / \mathrm{C}$ (111) with the $1 \times 1$ model. In the case of the $2 \times 1$ model, the $\pi$-bond length of the first C-layer atoms changes from $1.44 \AA$ to $1.52 \AA$. The elongation of the $\pi$-bond weakens itself. These structural characteristics explain well the change in the energetics and the stability obtained for the $\mathrm{Ni} / \mathrm{C}(111)$ surfaces.

Table 3.1 Relative energies (in units of $\mathrm{eV} /(1 \times 1$ surface) of the clean and Ni -covered C (111) surfaces; The surface (or interface) energy has been calculated with respect to the total energy of $1 \times 1$ model of each surface.

|  | $1 \times 1$ | $2 \times 1$ |
| :---: | :---: | :---: |
| clean $\mathrm{C}(111)$ | 0 | -0.78 |
| $\mathrm{Ni} / \mathrm{C}(111)$ | 0 | +0.30 |

### 3.3.2. Charge Analysis

To obtain physical insight into structural changes induced by the adsorption of Ni atoms on $\mathrm{C}(111)$, we also performed a charge analysis for $\mathrm{Ni} / \mathrm{C}(111)$ surfaces of the $1 \times 1$ and the $2 \times 1$ models. Fig. 3.2 shows the isosurface plot of the electron-density difference $\Delta \rho$ for the $\mathrm{Ni} / \mathrm{C}$ (111) surfaces of the $1 \times 1$ and the $2 \times 1$ models. In both models, a substantial rearrangement of electrons is observed around the Ni atoms. The significant accumulation of electrons in the region between Ni atoms and underlying C atoms is seen. Covalentlike $\mathrm{Ni}-\mathrm{C}$ bonds are formed thereby. In the case of the $1 \times 1$ model [Fig. 3.2 (a)], the adsorption of Ni atoms removes the dangling bonds of the surface C atoms through the formation of $\mathrm{Ni}-\mathrm{C}$ bonds. Besides, electron accumulation occurs between the second and the third C layers, strengthening the $\mathrm{C} 2-\mathrm{C} 3$ bond. In the case of the $2 \times 1$ model [Fig. 3.2 (b)], Ni atoms are located near the surface C atoms of the $\pi$-bonded chain and interact with the $2 p_{z}$ orbitals of the outermost C atoms. Depletion of electrons occurs in particular near the $\pi$ bonded chain region. This indicates the weakening of $\pi$-bonds that are important in the Pandey $\pi$-bonded chain structure and explains the thermodynamically more favorable formation of $\mathrm{Ni} / \mathrm{C}(111)$ with $1 \times 1$ model compared to that with the $2 \times 1$ model.

A Bader charge analysis [62-64] was also carried out to obtain information on the atomic charge states of $\mathrm{Ni} / \mathrm{C}(111)$. The results are shown in Table 3.2. When Ni atoms adsorb on C(111), for both $1 \times 1$ and $2 \times 1$ models, Ni atoms on $\mathrm{C}(111)$ are slightly positively
charged, while the first layer C atoms are more negatively charged, compared to the clean $C$ (111) surfaces. This indicates that although the $\mathrm{Ni}-\mathrm{C}$ bonds are mostly covalent, they have some ionic character. In the $1 \times 1$ model, the charge redistribution is also associated with the second and third C layers, which were relatively electrondepleted and positively charged before the Ni adsorption. From this result, it can be understood that before the Ni adsorbs, the electrons are removed from the bond between the second and third $C$ layers to stabilize the outermost C surface layer and after Ni adsorbs, Ni provides electrons for the interfacial $C$ layer instead of the second and third $C$ layers so that the second and third $C$ layers receive the electrons back. In the case of the $2 \times 1$ model, there is no large charge redistribution in the subsurface region, and it can be seen that electrons are transferred from the Ni only to the interfacial C1 layer.

## (a)


(b)


Figure 3.2 Isosurface plots of electron-density difference $\Delta \rho=$ $\rho_{\mathrm{Ni} / \mathrm{C}}-\rho_{\mathrm{C}}-\rho_{\mathrm{Ni}}$. Electron accumulation and depletion regions are denoted by yellow and blue, respectively. The isosurface levels are $\pm 0.007$ electrons/bohr ${ }^{3}$.

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Table 3.2 Bader charges (in units of $|e|$ ) in the geometry-optimized structures of the $1 \times 1$ and the Pandey $\pi$-bonded chain $2 \times 1$ models for clean and Ni -covered $\mathrm{C}(111)$ surfaces.

| Model | $1 \times 1$ |  |  | $2 \times 1$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Clean C(111) | $\mathrm{Ni} / \mathrm{C}(111)$ |  | Clean C(111) |  |
|  |  | $\mathrm{Ni} / \mathrm{C}(111)$ |  |  |  |
| Ni | -0.11 |  | +0.07 |  |  |
| C 1 | -0.15 | -0.18 |  | -0.02 |  |
| C 2 | +0.16 | +0.04 |  | -0.08 |  |
| C 3 | +0.02 | +0.06 | -0.02 | +0.01 |  |

### 3.3.3. Crystal Orbital Hamilton Population Analysis

To obtain chemical insights into the structural changes caused by the presence of the Ni surface layer on $\mathrm{C}(111)$, we calculated the pCOHP and integrated pCOHP (IpCOHP). Fig. 3.3 shows the pCOHPs and the IpCOHPs of various atomic bonds for the $1 \times 1$ and the $2 \times 1$ models for the clean and Ni -covered $\mathrm{C}(111)$ surfaces. In Fig. 3.3, pCOHP is displayed so that positive values represent bonding and negative values represent antibonding. The - IpCOHP at Fermi energy $E_{F}\left(-\mathrm{IpCOHP}_{\mathrm{F}}\right)$ used as a measure of bond strength is obtained by calculating the energy integral of -pCOHP up to Fermi energy $E_{F}$. The structural and charge analyses show that the favorable formation of the $1 \times 1$ diamond bulk-like $\mathrm{Ni} / \mathrm{C}(111)$ configuration is associated with the shortening of the $\mathrm{C} 2-\mathrm{C} 3$ bond length induced by the adsorption of the Ni surface atoms. The pCOHP analysis of $\mathrm{C} 2\left(2 p_{z}\right)-\mathrm{C} 3\left(2 p_{z}\right)$ bond for $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ shows that the additional formation of bonding states is induced in the range from -4 to -2 eV by the surface Ni atoms, compared to that for clean $1 \times 1 \mathrm{C}(111)$ [Fig. 3.3 (a) and (b)]. These additional bonding states increase the $-\mathrm{IpCOHP}_{\mathrm{F}}$ value from $2.87 \mathrm{eV}[1 \times 1$ clean $\mathrm{C}(111)$ ] to $3.35 \mathrm{eV}[1 \times 1 \mathrm{Ni} / \mathrm{C}(111)]$. This supports the strengthening of the $\mathrm{C} 2-\mathrm{C} 3$ bond by adsorption of the Ni surface atoms. Fig. 3.3(c) and (f) show the -pCOHP populations of the $\mathrm{Ni}\left(3 d_{z^{2}}\right)-\mathrm{C} 1\left(2 p_{z}\right)$ bonds for the $1 \times 1$ and the $2 \times 1$ models of $\mathrm{Ni} / \mathrm{C}(111)$ models of $\mathrm{Ni} / \mathrm{C}(111)$, respectively. Interestingly, it is found that the bonding -pCOHP peaks below $E_{F}$ for the $1 \times 1$

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$\mathrm{Ni} / \mathrm{C}(111)$ model are larger than those for the $2 \times 1$ model. As a result, the larger - IpCOHP $_{F}$ value of 1.11 eV for the $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ system is obtained compared to 0.60 eV for the $2 \times 1$ model of $\mathrm{Ni} / \mathrm{C}(111)$. This difference between the bonding states for the $1 \times 1$ and the $2 \times 1$ models of $\mathrm{Ni} / \mathrm{C}(111)$ further supports the favorable formation of the diamond bulk-like $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ structure. Fig. 3.3 (d) and (e) show the -pCOHP populations of the $\mathrm{C} 1\left(2 p_{z}\right)-\mathrm{C1}^{\prime}\left(2 p_{z}\right)$ bonds for the $2 \times 1$ models of clean $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$, respectively. For the $2 \times 1$ model of clean $\mathrm{C}(111)$, the -pCOHP peaks of the filled $\pi$-bonding and empty $\pi^{*}$ anti-bonding states are seen near $E_{F}$, whereas for the $2 \times 1$ model of $\mathrm{Ni} / \mathrm{C}(111)$, the peaks of the filled $\pi^{*}$ anti-bonding and partially empty $\pi$-bonding states are seen near $E_{F}$. The -pCOHP peaks near $E_{F}$ for the $2 \times 1$ model of $\mathrm{Ni} / \mathrm{C}(111)$ are much smaller than those for the $2 \times 1$ model of clean $\mathrm{C}(111)$. Very importantly, the $-\mathrm{IpCOHP}_{\mathrm{F}}$ value of the $2 \times 1$ model of $\mathrm{Ni} / \mathrm{C}(111)$ at 0.66 eV is a significant decrease from 1.48 eV of the $2 \times 1$ model of clean $\mathrm{C}(111)$. The decrease of 0.82 eV supports the weakening of the $\pi$-bonds, which plays a crucial role in destabilizing the $\pi$-bond chain structure. All these characteristics provide the electronic origin for the preference of the diamond bulklike $1 \times 1$ structure of the interfacial C atoms in $\mathrm{Ni} / \mathrm{C}(111)$.


Figure 3.3 Projected crystal orbital hamilton population (pCOHP) analysis for the chosen atomic bonds in the clean $\mathrm{C}(111)$ and the $\mathrm{Ni} / \mathrm{C}(111)$ systems: (a) C2 $\left.2 p_{z}\right)-\mathrm{C} 3\left(2 p_{z}\right)$ bond in the $1 \times 1$ model of clean C(111), (b) C2 $\left.2 p_{z}\right)-\mathrm{C} 3\left(2 p_{z}\right)$ and (c) $\mathrm{Ni}\left(3 d_{z^{2}}\right)-\mathrm{C} 1\left(2 p_{z}\right)$ bonds in the $1 \times 1$ model of $\mathrm{Ni} / \mathrm{C}(111)$, (d) $\mathrm{C} 1\left(2 p_{z}\right)-\mathrm{C} 1^{\prime}\left(2 p_{z}\right)$ bond in the $2 \times 1$ model of clean C(111), (e) $\mathrm{C} 1\left(2 p_{z}\right)-\mathrm{C} 1^{\prime}\left(2 p_{z}\right)$ and (f) $\mathrm{Ni}\left(3 d_{z^{2}}\right)-$ $\mathrm{C} 1\left(2 p_{z}\right)$ bonds in the $2 \times 1$ model of $\mathrm{Ni} / \mathrm{C}(111)$. The values of IpCOHP at Fermi energy $E_{F}$ ( - IpCOHPF) are presented for comparison of the bond strength. The Fermi energy is taken as energy zero.

### 3.3.4. Surfactant-mediated Growth

Next, for the continuous growth of diamond films on the $\mathrm{Ni}-$ covered $1 \times 1 \mathrm{C}(111)$ surface, we investigate the kinetic processes required for carbon atoms to incorporate into the C substrate of the $1 \times 1$ model underneath the Ni layer. This is a key kinetic step in the crystal growth process widely known as surfactant-mediated growth [65-68], in which the surfactant atoms are retained on the growing surface by the exchange of the surfactant atoms and the incoming source C atoms during the crystal growth. Fig. 3.4 shows the incorporation process of the C adatom into site U underneath the surface Ni layer. Upon adsorption of the C adatom on $\mathrm{Ni} / \mathrm{C}(111)$, our total energy calculations show that bridge site B is the most stable surface adsorption site. We found that the Ni adsorption at site U is stable and that site U is more stable than site B by -0.49 eV . This indicates that the C atoms adsorbed on the Ni surfactant layer thermodynamically penetrate the surfactant layer and stably bond to the C atoms underneath the Ni surfactant layer. This naturally leads to an examination of the penetration pathway $\mathrm{B} \rightarrow \mathrm{U}$. The activation energy for the process $B \rightarrow U$ was calculated using the climbing image nudged elastic band method (CI-NEB) [69] and the value is 0.88 eV . The Relative energy curve along the penetration pathway is shown in Fig. 3.5. Considering typical growth temperatures in diamond synthesis with Ni catalysts, the result of the calculated activation energy suggests the plausible growth of diamond by the surfactant-mediated growth mode.


Figure 3.4 Penetration pathway for a C atom on $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ starting from surface bridge site $B$, ending in site $U$, underneath the surface Ni layer. Site TS is the transition state for the process $B \rightarrow U$.

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Figure. 3.5 Relative energy curve along the penetration pathway for a C atom on $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ starting from surface bridge site B (image 0), ending in site $U$ (image 10). The transition state TS (image 5) for the process $B \rightarrow U$ has the activation energy of 0.88 eV relative to site $B$.

### 3.4. Conclusion

In this chapter, based on ab-initio total-energy and electronic structure calculations, we investigated the physical roles of Ni adsorbed at the surface of $C$ (111) in addition to the carbon-solvency role of Ni in the catalytic growth of diamond. The total energy calculations demonstrate a structural transformation from the reconstructed structure with the Pandey $\pi$-bonded chains back to the diamond bulk-like structure at the Ni/C interface. The electronic structure calculations show that it is originated from (i) strengthening of the C2-C3 bond, (ii) the covalent-like interaction of Ni with the dangling bond of the interfacial C 1 atom in the $1 \times 1$ $\mathrm{Ni} / \mathrm{C}(111)$ system, and (iii) weakening of the $\pi$-bond of the Pandey $\pi$-bonded chain structure of $\mathrm{Ni} / \mathrm{C}(111)$. Thereby, the process temperature and pressure for diamond growth with a Ni catalyst can be lowered due to the diamond bulk-like structure, whereas for diamond growth without catalytic metals such as Ni , extreme conditions [70] of about 125 kbar and 3000 K are required due to the necessity of the deformation of the strong carbon $\pi$-bond. Further kinetic calculations using the CI-NEB method reveal that the carbon adatom as a source of diamond growth can penetrate a near-surface interfacial site to form a $\mathrm{C}-\mathrm{C}$ bond. As a result, the catalytic Ni atoms enable surfactant-mediated processes for the continuous growth of diamond. These reactive behaviors of Ni on $\mathrm{C}(111)$, which have not been considered so far, are expected to provide the underlying
mechanism in the interface of $\mathrm{Ni} / \mathrm{C}(111)$ in diamond synthesis via Ni catalysts. Our findings for the catalytic growth processes of diamond on C(111) can also provide important information for research works of chemical vapor deposition growth of diamond films to fabricate electronic devices like the next-generation power devices in microelectronics.

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# Chapter 4. Phonon spectra of clean and $\mathrm{Ni}-$ terminated diamond (111) surfaces 

### 4.1. Introduction

The growth of diamonds has attracted a great deal of interest due to its technological importance in a wide range of applications, such as machine tools, optical coatings, high-temperature electronics, and next-generation power devices [71-76]. The C(111) surface in diamond is a growth surface and natural cleavage plane with lower surface formation energy than other surfaces. Its surface structure is known to play an important role in determining the morphology and quality of the growing diamond, as well as many other physical properties [35-37]. Although the detailed atomic geometry of the reconstructed clean $\mathrm{C}(111)$ surface is still controversial, most experimental and theoretical studies $[38,39]$ support the Pandey $\pi$-bonded $2 \times 1$ chain model of $\mathrm{C}(111)$ [Fig. 4.1(c)]. The $s p^{2}$ surface bonding character in the $\pi$-bonded chain model of $2 \times 1$ reconstructed $\mathrm{C}(111)$ would prevent C adatoms from making $s p^{3}$ bonds for the growth of diamond, instead of promoting the growth of undesired graphite.

To overcome this obstacle to diamond growth, diamond synthesis has typically been conducted using catalytic metals such as $\mathrm{Fe}, \mathrm{Ni}$,
and Co [21, 22]. Until recently, Ni has been the main catalytic metal element used [42-46]. In the previous chapter, we theoretically studied the microscopic role of catalytic metal Ni in the growth calculations. The results showed that surface Ni atoms can enhance the formation of a thermodynamically stable $\mathrm{Ni}-\mathrm{C}$ interface with a diamond bulk-like $1 \times 1$ structure, which is essential for the formation of $s p^{3}$-bonded carbon in the diamond. Further investigation showed that this feature originates originated from (i) strengthening of the $\mathrm{C} 2-\mathrm{C} 3$ bond, (ii) the covalent-like interaction of Ni with the dangling bond of the interfacial C 1 atom in the $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ system, and (iii) weakening of the $\pi$-bond of the Pandey chain structure of $\mathrm{Ni} / \mathrm{C}(111)$. These findings provide a good explanation for the efficacy of Ni as a catalyst for diamond growth.

Despite these studies, experimental information on the structures, bonding, and dynamics of $\mathrm{Ni} / \mathrm{C}(111)$ surfaces remains limited. In particular, surface vibrational measurements are very useful for studying diamond surfaces. There have been no experimental or theoretical works on the vibrational properties of the growth surfaces of diamond in the presence of catalytic metal Ni. In this chapter, the phonon densities of states (ph-DOSs) of clean and Ni -terminated $\mathrm{C}(111)$ surfaces with $1 \times 1$ and $2 \times 1$ surface structures were studied by conducting ab-initio calculations based on density functional perturbation theory (DFPT) [77, 78]. The calculation revealed discernible features in the vibrational spectra of the $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$ surfaces depending on the surface and interface structures. This could play a significant role in
experimentally verifying the atomic structures at $\mathrm{Ni} / \mathrm{C}(111)$, as well as understanding the microscopic mechanism of the catalytic metal ( Ni ) in diamond growth.


Figure 4.1 Top and side views of the clean and Ni -terminated C (111) surfaces: (a) $1 \times 1 \mathrm{C}(111),($ (b) $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, (c) $2 \times 1 \mathrm{C}(111)$, and (d) $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$. Large grey circles represent Ni atoms, and small brown circles represent C atoms. Cn and $\mathrm{Cn}^{\prime}$ denote the C atoms in the $\mathrm{n}-\mathrm{th} \mathrm{C}$ layer. The black lines denote the $2 \times 1$ surface unit cell used in the calculations.

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### 4.2. Computational Details

All calculations were performed using the plane-wave pseudopotential method within the framework of spin-unpolarized density functional theory (DFT), as implemented in the Vienna $A b-$ initio Simulation Package (VASP) code [47, 49]. For the exchangecorrelation interactions of electrons, the Perdew-Burke-Ernzerhof (PBE) formation within the generalized gradient approximation (GGA) was used [50]. The pseudopotentials for electron-ion interactions were described using the projector augmented-wave (PAW) method [51]. The electronic wave functions were expanded using a planewave basis set with an energy cutoff of 400 eV .

For the calculations of the clean and Ni -terminated $\mathrm{C}(111)$ surfaces, we used a supercell with a repeating slab structure consisting of six atomic C layers with a $20 \AA$ vacuum region along the surface normal direction, and a $2 \times 1$ rectangular surface unit cell in the lateral ( x and y ) directions as shown in Fig. 4.1. The Ni layer in $\mathrm{Ni} / \mathrm{C}(111)$ was adsorbed only on the upper side of the slab. The bottom $C$ atoms of the slab were passivated by hydrogen atoms. A theoretical PBE equilibrium lattice constant ( $a_{0}=3.55 \AA$ ) for bulk diamond was used. The $\mathbf{k}$-point integration was conducted with a $6 \times 10 \times 1$ grid in the Brillouin zone (BZ) of the supercell. To decide the atomic positions of the H atoms in $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$, a twosided surface of $H$-terminated $C(111)$ [H/C(111)] was used and only the geometry of the H atoms was optimized. The obtained $\mathrm{C}-\mathrm{H}$
distance was used to create the bottom H -terminated surface. All atoms in the slab were relaxed, except for the bottom C and H atoms. Geometry optimization was conducted until the remaining forces of the atoms were smaller than $0.01 \mathrm{eV} / \AA$.

To calculate the ph-DOSs of C(111) and $\mathrm{Ni} / \mathrm{C}(111)$, we used the PHONOPY code, which utilizes the force constants generated by performing DFPT calculations implemented in VASP [79]. A $6 \times 10 \times 1$ q-point grid was applied to calculate the surface ph-DOSs.

### 4.3. Results and Discussion

### 4.3.1. Phonon DOSs

We calculated the phonon spectra from the geometry-optimized atomic structures of $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$. Fig. 4.2 shows the simulated $\mathrm{ph}-\mathrm{DOSs}$ for the $1 \times 1$ and $2 \times 1$ models of $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$, where the phonon eigenvalues were broadened using a Gaussian function of width $30 \mathrm{~cm}^{-1}$. The phonon spectra of the clean $C$ (111) surfaces are the projected ph-DOS of the three upper C layer atoms of the model slab, whereas the projected ph-DOS of the $\mathrm{Ni} / \mathrm{C}$ (111) surfaces include the surface Ni layer atoms. The projected ph-DOSs exhibit significant vibrational features associated with the surface structures of $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$.

The ph-DOS of $1 \times 1$ clean $C(111)$ shows three bands in the regions of $200-400,400-1000$, and $1000-1400 \mathrm{~cm}^{-1}$, with peak

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positions located at 360, 690, and $1240 \mathrm{~cm}^{-1}$, respectively [Fig. 4.2(a)]. The ph-DOS of $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ shows an intense band below $300 \mathrm{~cm}^{-1}$ and a broad band in the region of $300-1400 \mathrm{~cm}^{-1}$, with respective peaks positioned at 150 and $1200 \mathrm{~cm}-1$ [Fig. 4.2 (b)]. The ph-DOS of $2 \times 1$ clean C (111) shows two bands in the regions of 300-910 and 910-1400 $\mathrm{cm}^{-1}$ [Fig. 4.2 (c)], consistent with previous theoretical and experimental results [80-82]. The two main peaks are at 750 and $1180 \mathrm{~cm}^{-1}$, respectively. The $\mathrm{ph}-\mathrm{DOS}$ of $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ shows an intense band below $300 \mathrm{~cm}^{-1}$ and a broad band in the region of $300-1400 \mathrm{~cm}^{-1}$ [Fig. 4.2 (d)], which has a shape distinct from that of $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ when viewed in detail. The two peak positions are located at 180 and $1040 \mathrm{~cm}^{-1}$, respectively.

To obtain more detailed information on the phonon spectra, we also investigated the surface normal and in-plane vibrations of the topmost surface two-layer C atoms (C1 and C2). In Fig. 4.2, the surface-normal (z-directional) modes are indicated by the blue dotted line, while the surface in - plane ( $x-$ and $y$-directional) modes are indicated by the red dashed line. For $1 \times 1$ clean $\mathrm{C}(111)$, the lower $\mathrm{ph}-\mathrm{DOS}$ band in the range of $200-400 \mathrm{~cm}^{-1}$ consists mainly of the surface normal modes of C 1 and C 2 . The middle band in the range of 400-1000 $\mathrm{cm}^{-1}$ consists of a mixture of the surface normal and in-plane modes, and the upper band in the range of 1000-1400 $\mathrm{cm}^{-1}$ consists only of the surface in-plane modes [Fig. 4.2(a)]. The surface normal and in-plane modes have phonon peaks at 360 and $1270 \mathrm{~cm}^{-1}$, respectively. For $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, the lower part of the broad band in the range of $300-1100 \mathrm{~cm}^{-1}$ consists of a mixture of
the surface normal and in-plane modes, and the upper part in the range of $1100-1400 \mathrm{~cm}^{-1}$ consists only of the surface in-plane modes [Fig. 4.2(b)]. The surface normal and in-plane modes have phonon peaks at 990 and $1200 \mathrm{~cm}^{-1}$, respectively. Compared with $1 \times 1$ clean $\mathrm{C}(111)$, the surface normal peak of $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ is significantly higher by $630 \mathrm{~cm}^{-1}$, while the surface in-plane peak shows little change. For $2 \times 1$ clean $\mathrm{C}(111)$, the lower band in the range of $310-910 \mathrm{~cm}^{-1}$ consists of a mixture of the surface normal and in-plane modes, and the upper band in the range of 910-1400 $\mathrm{cm}^{-1}$ consists mainly of the surface in-plane modes [Fig. 4.2(c)]. The surface normal and in-plane modes have phonon peaks at 750 and $1180 \mathrm{~cm}^{-1}$, respectively. Compared with $1 \times 1$ clean $\mathrm{C}(111)$, the surface normal peak of $2 \times 1$ clean $C(111)$ is higher, by $390 \mathrm{~cm}^{-1}$. For $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, the lower part of a broad band in the range of $300-900 \mathrm{~cm}^{-1}$ consists of a mixture of the surface normal and inplane modes, and the upper part in the range of $900-1400 \mathrm{~cm}^{-1}$ consists mainly of the surface in-plane modes [Fig. 4.2(d)]. The surface normal and in-plane modes have phonon peaks at 810 and $1050 \mathrm{~cm}^{-1}$, respectively. Compared with $2 \times 1$ clean $\mathrm{C}(111)$, the surface normal peak position of $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ is higher (by $60 \mathrm{~cm}^{-}$ ${ }^{1}$ ) and the surface in - plane peak position is lower (by $-130 \mathrm{~cm}^{-1}$ ). Compared with $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, the surface normal and in-plane phonon peak positions of $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ are lower, by -180 and $150 \mathrm{~cm}^{-1}$, respectively.

For the $1 \times 1$ and $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ surfaces, we also investigated the vibrations localized on the surface Ni atoms. In Fig.
4.2 (b) and (d), the ph-DOSs of the Ni -localized surface vibrational modes are indicated by the orange dash-dotted line. The ph-DOSs of $\mathrm{Ni} / \mathrm{C}(111)$ clearly show that the ph-DOS band in the region below $300 \mathrm{~cm}^{-1}$ consists mainly of the vibrational modes of the surface Ni atoms. For more detailed analysis, we also investigated the surface normal and in-plane vibrations of the surface Ni atoms. Fig. 4.3 shows the enlarged ph-DOSs in the region below $300 \mathrm{~cm}^{-1}$ with the Ni -localized ph-DOSs of the surface normal and in-plane vibrational modes. Here, the surface normal modes are indicated by the cyan dotted line, while the surface in-plane modes are indicated by the orange dashed line. For $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, the surface in-plane and normal modes have peaks at 140 and $210 \mathrm{~cm}^{-1}$, respectively [Fig. 4.3 (a)]. For $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, the surface in-plane modes have a peak at $160 \mathrm{~cm}^{-1}$, which is higher by $20 \mathrm{~cm}^{-1}$ than that of $1 \times 1$ $\mathrm{Ni} / \mathrm{C}(111)$ [Fig. $4.3(\mathrm{~b})$ ]. The surface in-plane band looks broader than that of $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$. The surface normal modes have a peak at $190 \mathrm{~cm}^{-1}$, which is lower (by $-20 \mathrm{~cm}^{-1}$ ) than that of $1 \times 1$ $\mathrm{Ni} / \mathrm{C}(111)$. As a result, the positions of the surface in-plane and normal peaks of $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ are closer to each other than those in $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, which leads to a sharp peak at $180 \mathrm{~cm}^{-1}$ in the total ph-DOS of the $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ surface.


Figure 4.2 Calculated surface phonon densities of states (ph-DOSs) of $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$. The black solid line represents the surface total ph-DOSs of C(111) and Ni/C (111). Here, the phonon spectra of $\mathrm{C}(111)$ are the projected $\mathrm{ph}-\mathrm{DOSs}$ of the three upper C layer atoms of the model slab, whereas the phonon spectra of $\mathrm{Ni} / \mathrm{C}(111)$ also include the surface Ni atoms. The blue dotted and the red dashed lines represent the surface normal ( $z$-directional) and the in-plane ( x - and y -directional) vibrational modes of the topmost surface two-layer C atoms (C1 and C2), respectively. The orange dashdotted line represents the vibrational modes of the surface Ni atoms. In the calculations, the phonon eigenvalues were broadened using a Gaussian function of width $30 \mathrm{~cm}^{-1}$.


Figure 4.3 Enlarged ph-DOS bands in the region below $300 \mathrm{~cm}^{-1}$ for $\mathrm{Ni} / \mathrm{C}(111)$. The black solid line represents the projected phDOSs of the three upper C layers and surface Ni atoms of the model slab. The cyan dotted and the orange dashed lines represent the surface normal and the in-plane vibrational modes of the surface Ni atoms, respectively. In the calculations, the phonon eigenvalues were broadened using a Gaussian function of width $30 \mathrm{~cm}^{-1}$.

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### 4.3.2. Phonon modes

Next, we investigated the frequencies and corresponding representations of surface phonon modes in the clean and $\mathrm{Ni}-$ terminated $\mathrm{C}(111)$ surfaces. Their vibrational assignments are presented in Tables 4.1 and 4.2, and the vibrations are described in Figs. 4.4 and 4.5 . In the $1 \times 1$ clean $C(111)$ surface, the lower phonon band involving the surface normal modes in the region 200$400 \mathrm{~cm}^{-1}$ has rocking -1 , bouncing -1 , and rocking -2 modes at 317 , 375 , and $392 \mathrm{~cm}^{-1}$, respectively (Table 4.1). These modes are illustrated in Fig. 4.4 (a), (b), and (c), respectively. In the rocking-1 mode, C1 and C2 atoms move in phase with each other and out of phase with respect to the $\mathrm{C}^{\prime}$ and $\mathrm{C}^{\prime}$ atoms. The vibrational amplitude of C1 is larger than that of C2. This mode shows the characteristics of $\mathrm{C} 1-\mathrm{C} 2$ bond bending and $\mathrm{C} 2-\mathrm{C} 3$ bond stretching. In the bouncing-1 mode, all C1 and C2 atoms move in phase and bounce with respect to the C3 atom. This mode shows the characteristic modification of the $\mathrm{C} 2-\mathrm{C} 3$ bond length. In the rocking2 mode, the C1 and C2 atoms move out of phase with each other and the $\mathrm{C} 1(\mathrm{C} 2)$ atom moves out of phase with respect to the $\mathrm{C}^{\prime}\left(\mathrm{C} 2^{\prime}\right)$ atom. The vibrational amplitude of C 2 is larger than that of C 1 . This mode shows the characteristic $\mathrm{C} 1-\mathrm{C} 2$ bond bending and $\mathrm{C} 2-\mathrm{C} 3$ bond stretching. The middle phonon band in the range of $400-1000 \mathrm{~cm}^{-1}$ involves the surface normal modes that are more associated with the subsurface C atoms, such as the $\mathrm{C} 2-\mathrm{C} 3$ stretching $-1, \mathrm{C} 2-\mathrm{C} 3$ stretching-2, and bouncing-2 modes at 524, 699, and $811 \mathrm{~cm}^{-1}$,
respectively (Table 1). These modes are illustrated in Fig. 4.4(d), (e), and (f), respectively.

In the $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ surface, the surface normal phonon modes of the C atoms are shifted towards a higher frequency region compared with that of $1 \times 1$ clean $\mathrm{C}(111$ ) [Fig. 4.2(a) and (b)]. Bouncing-1, rocking-1, rocking-2, C2-C3 stretching-2, C2-C3 stretching-1, and bouncing-2 modes were observed at 546, 661, $786,833,907$, and $1072 \mathrm{~cm}^{-1}$, respectively. This hardening in the surface normal phonon spectra is coincident with the structural changes induced by the adsorption of $1 \times 1 \mathrm{Ni} / \mathrm{C}$ (111) [Fig. 3.1 and Chapter 3]. Compared with the $1 \times 1$ clean $C(111)$ surface, the previous study for $1 \times 1 \mathrm{Ni} / \mathrm{C}$ (111) showed that the C2-C3 bond length significantly changes from 1.70 to $1.59 \AA$, close to the bulkdiamond bond length of $1.54 \AA$. As a result of such structural changes due to the adsorption of Ni, it is more difficult to deform the C1-C2 and the $\mathrm{C} 2-\mathrm{C} 3$ bonds compared with $1 \times 1$ clean $\mathrm{C}(111)$.

For the phonon modes of the surface Ni atoms in $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, the surface in-plane phonon band has Ni sliding - $\mathrm{x}, \mathrm{Ni}$ sliding- y , Ni twisting, and Ni scissoring modes at $65,83,160$, and $226 \mathrm{~cm}^{-1}$, respectively, while the surface normal band has Ni stretching -1 and -2 modes at 232 and $250 \mathrm{~cm}^{-1}$, respectively (Table 4.1). These modes are illustrated in Fig. $4.4(\mathrm{~g})$, (h), (i), (j), (k), and (l), respectively.

In the $2 \times 1$ clean $C(111)$ surface, the surface normal band in the region of $300-910 \mathrm{~cm}^{-1}$ has bouncing-1, bouncing-2, rocking-1, and rocking -2 modes at $405,618,705$, and $902 \mathrm{~cm}^{-1}$, respectively

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(Table 4.2). The phonon frequencies are higher than those of $1 \times 1$ clean $\mathrm{C}(111)$. The surface in-plane phonon band in the region of $910-1400 \mathrm{~cm}^{-1}$ has stretching -1 and -2 modes along the chainnormal (x) direction at 1167 and $1320 \mathrm{~cm}^{-1}$, respectively (Table 4.2). These modes are illustrated in Fig. 4.5 (a), (b), (c), (d), (e), and (f), respectively.

In the $2 \times 1 \mathrm{Ni} / C(111)$ surface, the surface normal band of the $C$ atoms is shifted towards a higher frequency region compared with that of $2 \times 1$ clean $C(111)$ [Fig. 4.2(c) and (d)]. Bouncing-1, bouncing -2 , rocking -1 , and rocking -2 modes were observed at 500, 650, 835 , and $1052 \mathrm{~cm}^{-1}$, respectively (Table 4.2). The shift in the surface normal band is ascribed to the hindered motion of the C atoms caused by the adsorption of Ni on $2 \times 1 \mathrm{C}(111)$. However, this effect is not as strong as the shift observed between the $1 \times 1$ models of $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$, as only a small change in the $\mathrm{C} 2-\mathrm{C} 3$ bond length occurs between the $2 \times 1$ models of $\mathrm{C}(111)$ and $\mathrm{Ni} / \mathrm{C}(111)$. In contrast to the surface normal band, the surface in-plane band is shifted towards a lower frequency region compared with that of $2 \times 1$ clean C(111) [Fig. 4.2 (c) and (d)]. Chain-normal stretching -1 and -2 modes were observed at 1100 and $1162 \mathrm{~cm}^{-1}$, respectively, which are lower by -67 and $-158 \mathrm{~cm}^{-1}$ than the corresponding values for $2 \times 1$ clean C(111). Such softening in the surface in - plane modes of $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ is coincident with the $\pi$-bond weakening induced by the adsorption of Ni on $2 \times 1 \mathrm{C}(111)$. In a previous chapter, this was explained by charge transfer from the Ni atoms to the antibonding $\pi^{*}$ state of the surface C -chain atoms, leading to elongation
of the topmost $\mathrm{C} 1-\mathrm{C} 1$ ' chain bond length from $1.44 \AA[\mathrm{C}(111)]$ to $1.52 \AA[\mathrm{Ni} / \mathrm{C}(111)]$.

For the phonon modes of the surface Ni atoms in $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, the surface in - plane phonon band has Ni sliding -x , Ni sliding $-\mathrm{y}, \mathrm{Ni}$ twisting, and Ni scissoring modes at $79,79,175$, and $233 \mathrm{~cm}^{-1}$, respectively (Table 4.2). The surface normal band has Ni stretching-1 and -2 modes at 198 and $201 \mathrm{~cm}^{-1}$, respectively (Table 4.2). These modes are illustrated in Fig. 4.5 (g), (h), (i), (l), (j), and (k), respectively. The frequencies of the Ni twisting and scissoring modes in $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ are higher than those in $1 \times 1$ $\mathrm{Ni} / \mathrm{C}(111)$, while the frequencies of the Ni stretching-1 and -2 modes are lower than those of $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$. Softening in the surface normal Ni stretching modes can explain the weak $\mathrm{Ni}-\mathrm{C}$ bond strength in the $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ surface compared with $1 \times 1$ Ni/C(111) [Chapter 3].

Table 4.1 Calculated frequencies and corresponding representations of surface phonon modes in the clean and Ni -terminated $\mathrm{C}(111)$ surfaces with $1 \times 1$ surface structures.

| Frequency $\left(\mathrm{cm}^{-1}\right)$ | Representation | Fig. 4.4 |
| :--- | :--- | :--- |
|  | $1 \times 1$ clean C(111) |  |
| 317 | rocking-1 | (a) |
| 375 | bouncing-1 | (b) |
| 392 | rocking-2 | (c) |
| 524 | C2-C3 stretching-1 | (d) |
| 699 | C2-C3 stretching-2 | (e) |
| 811 | bouncing-2 | (f) |
|  | $1 \times 1$ Ni/C (111) |  |
| 65,83 | Ni sliding-x, sliding-y | (g), (h) |
| 160 | Ni twisting | (i) |
| 226 | Ni scissoring | $(\mathrm{j})$ |
| 232 | Ni stretching-1 | $(\mathrm{k})$ |
| 250 | Ni stretching-2 | $(\mathrm{l})$ |
| 546 | bouncing-1 |  |
| 661 | rocking-1 |  |
| 907 | rocking-2 |  |
| 833 | C2-C3 stretching-2 |  |
| 907 | C2-C3 stretching-1 |  |
| 1072 | bouncing-2 |  |

Table 4.2 Calculated frequencies and corresponding representations of surface phonon modes in the clean and Ni -terminated $\mathrm{C}(111)$ surfaces with $2 \times 1$ surface structures.

| Frequency ( $\mathrm{cm}^{-1}$ ) | Representation | Fig. 4.5 |
| :---: | :---: | :---: |
| $2 \times 1$ clean C (111) |  |  |
| 405 | bouncing - 1 | (a) |
| 618 | bouncing-2 | (b) |
| 705 | rocking-1 | (c) |
| 902 | rocking-2 | (d) |
| 1167 | chain-normal stretching-1 | (e) |
| 1320 | chain-normal stretching-2 | (f) |
| $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ |  |  |
| 79,79 | Ni sliding -x , sliding -y | (g), (h) |
| 175 | Ni twisting | (i) |
| 198 | Ni stretching-1 | (j) |
| 201 | Ni stretching-2 | (k) |
| 233 | Ni scissoring | (1) |
| 500 | bouncing-1 |  |
| 650 | bouncing-2 |  |
| 835 | rocking-1 |  |
| 1052 | rocking-2 |  |
| 1100 | chain-normal stretching-1 |  |
| 1162 | chain-normal stretching-2 |  |

(a)
(b)
(c)
(d)




(e)


(g)

(h)

(f)
(i)

(j)

(k)

(1)


Figure 4.4 Representations of surface phonon modes of clean and $\mathrm{Ni}-$ terminated $\mathrm{C}(111)$ with $1 \times 1$ surface structures, corresponding to the selected frequencies in Table 4.1. Arrows indicate the amplitude and direction for each atom in each phonon mode. (a) Rocking - 1, (b) bouncing-1, (c) rocking-2, (d) C2-C3 stretching-1, (e) C2-C3 stretching-2, (f) bouncing-2, (g) Ni sliding-x, (h) Ni sliding-y, (i) Ni twisting, (j) Ni scissoring, (k) Ni stretching-1, and (1) Ni stretching-2.
(a)
(b)
(c)
(d)




(e)
(f)
(g)
(h)




(i)
(j)
(k)
(1)





Figure 4.5 Representations of surface phonon modes of clean and $\mathrm{Ni}-$ terminated C (111) with $2 \times 1$ surface structures, corresponding to the selected frequencies in Table 4.2. Arrows indicate the amplitude and direction for each atom in each phonon mode. (a) Bouncing-1, (b) bouncing-2, (c) rocking-1, (d) rocking-2, (e) chain-normal stretching-1, (f) chain-normal stretching-2, (g) Ni sliding-x, (h) Ni sliding-y, (i) Ni twisting, (j) Ni stretching-1, (k) Ni stretching2, and (1) Ni scissoring.

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### 4.4. Conclusion

Using DFPT calculations, we investigated the ph-DOS of clean and Ni-terminated $\mathrm{C}(111)$ surfaces with $1 \times 1$ and $2 \times 1$ surface structures. For the $1 \times 1$ clean $C(111)$ surface, the $\mathrm{ph}-\mathrm{DOS}$ showed three bands in the regions of $200-400,400-1000$, and 1000-1400 $\mathrm{cm}^{-1}$. The ph-DOS peaks were positioned at 360,690 , and $1240 \mathrm{~cm}^{-}$ ${ }^{1}$, respectively. The $\mathrm{ph}-\mathrm{DOS}$ of $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ showed an intense band and a broad band with respective peaks at 150 and $1200 \mathrm{~cm}^{-1}$. The ph-DOS of $2 \times 1 \mathrm{C}$ (111) showed two bands, whose peaks were positioned at 750 and $1180 \mathrm{~cm}^{-1}$, respectively. The $\mathrm{ph}-\mathrm{DOS}$ of $2 \times 1$ $\mathrm{Ni} / \mathrm{C}(111)$ showed an intense band and a broad band with respective peaks at 180 and $1040 \mathrm{~cm}^{-1}$, whose ph-DOS shape looked different from that of $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$. Further detailed analyses of various surface normal and in-plane modes of the surface carbon and Ni atoms were also conducted. For $\mathrm{Ni} / \mathrm{C}(111)$, the vibrations of the surface Ni atoms formed an intense band in the low frequency region below $300 \mathrm{~cm}^{-1}$, whereas the vibrations of the surface and subsurface $C$ atoms formed a broad band in the frequency region of 300$1400 \mathrm{~cm}^{-1}$. The previous chapter showed the favorable formation of the diamond bulk-like structure for $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, and the weakening of the surface $\pi$-bonds for $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$, when C(111) was covered with Ni. The vibrational changes with adsorption of Ni on $\mathrm{C}(111)$ agreed well with the structural changes and $\pi$-bond weakening induced by the surface Ni atoms in $\mathrm{Ni} / \mathrm{C}$ (111) with respect
to the clean $C(111)$ surfaces. The differences in the ph-DOSs obtained in this study are expected to be useful for experimentally identifying the interface structure of $\mathrm{Ni} / \mathrm{C}(111)$, which is important for understanding the catalytic effect of metal Ni in diamond growth processes.

# Chapter 5. Surface catalytic effect of transition metals on diamond (111) and their periodic trends 

### 5.1. Introduction

Since General Electric (GE) succeeded in synthesizing diamond for the first time in 1955 [21], the growth of diamond has attracted a lot of interest due to their technological importance in a wide range of applications, such as machine tools, optical coatings, hightemperature electronics, and next-generation power devices [7176]. Diamond has been synthesized by use of catalytic elements, such as $\mathrm{Fe}, \mathrm{Co}$, and $\mathrm{Ni}[22]$ and other transition elements [24, 83]. Until recently, these transition metals are important catalysts [42-46]. The metal catalysts have been known to become liquid phase forming a thin film on the diamond surface and exhibit appreciable solubility of carbon. There have been many studies on the solubility effect, but there are few studies on what happens on the surface. In some experiments, the diamond formation was found to be promoted even in the low carbon solubility [22-24], and some scientists think that the role of catalytic metals on the surface should be further elucidated.

The $\mathrm{C}(111)$ surface, as the most stable surface of the diamond,
plays an important role in determining the morphology of the growing diamond and its properties [35-37]. As for the surface structure of clean $\mathrm{C}(111)$, although the detailed atomic structure is still controversial, most experimental and theoretical studies [38, 39] support the Pandey $\pi$-bonded chain model as a stable surface structure. The $s p^{2} \pi$-bonded chain structure of the $2 \times 1$ reconstructed surface would prevent the surface $C$ atoms from forming $S p^{3}$ bonds and would be more favorable to the growth of graphite than to that of diamond. Thereby, in the high pressure and high temperature (HPHT) process, without catalytic metals, extreme conditions [70] of about 125 kbar and 3000 K would be required due to the necessity of the deformation of the strong surface $\pi$-bond. In the field of thin-film diamond growth, many studies have been conducted on elements that remove the $\pi$-bond of the Pandey chain on $C$ (111) through surface reaction $[58,84-86]$. But, no studies have been reported that consider surface effects of transition metals in the HPHT system.

In Chapters 3 and 4, we investigated the microscopic role of Ni metal on the surface theoretically through ab-initio electronic and vibrational calculation. These results show that Ni addition can form a thermodynamically stable $\mathrm{Ni}-\mathrm{C}$ interface with a $1 \times 1$ diamond bulk-like structure. Further kinetic calculations using the CI-NEB method reveal that the carbon adatom as a source of diamond growth can penetrate the Ni layer into a subsurface to form a $\mathrm{C}-\mathrm{C}$ bond. As a result, the catalytic Ni atoms enable surfactant-mediated processes for the continuous growth of diamond. These reactive

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behaviors of Ni metals on C(111) surface suggested the microscopic mechanism of the surface catalytic effect of Ni on diamond synthesis.

In this chapter, we investigated the surface effect of all transition metals using the electronic total energy calculations based on $a b-$ initio density functional theory. The calculated results showed significant changes in interfacial energies and structures of $\mathrm{M} / \mathrm{C}$ (111) and show an important periodic trend. These results well explain the previous results of many experiments and will be information for the future catalytic metal selection and alloy design for diamond growth.

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### 5.2. Computational Details

All calculations are carried out using the plane-wave pseudopotential method within the framework of the spinunpolarized density functional theory (DFT) as implemented in the Vienna $A b$-initio Simulation Package (VASP) code [47, 49]. For the exchange-correlation interactions of electrons, the Perdew-BurkeErnzerhof (PBE) expression within the generalized gradient approximation (GGA) was used [50]. The electron-ion interactions were described by employing the projector augmented-wave (PAW) method [51]. The electronic wave functions were expanded by a plane wave basis set with an energy cutoff of 400 eV .

For the calculations of the transition metal-terminated C (111) surfaces $[M / C(111)]$, we used a supercell of a repeating slab structure consisting of six atomic C layers with a $20 \AA$ vacuum region along the surface normal direction and a $2 \times 1$ rectangular surface unit cell in the lateral ( x and y ) directions. Fig. 5.1 shows the surface structures of $M / C(111)$ with $1 \times 1$ and $2 \times 1$ models we used in this study.

The M layer in M/C (111) was adsorbed only on the upper side of the slab and the bottom $C$ atoms of the slab were passivated by hydrogen atoms. A theoretical equilibrium lattice constant $\left(a_{0}=\right.$ $3.55 \AA$ ) of diamond in bulk was used for the slab. The $k$-point integration was done with a $6 \times 10 \times 1$ grid in the Brillouin zone (BZ) of the supercell. To decide the atomic positions of the $H$ atoms in

M/C(111), the two-sided surface of $H$-terminated $\mathrm{C}(111)[\mathrm{H} / \mathrm{C}(111)]$ was used and only the geometry of the H atoms was optimized. The obtained $\mathrm{C}-\mathrm{H}$ distance was used to make the bottom H -terminated surface. All M and C atoms were fully relaxed, except for the bottommost C and H atoms. It is herein also noted that for the left-side metals (Sc, Ti, V, Y, Zr, and Hf) of the periodic table, the $1 \times 1$ and $2 \times 1 \mathrm{M} / \mathrm{C}(111)$ interfaces have a tendency to form interface structures that deviated from the M/C(111) interface structures of Fig. 5.1 obtained for the other metal atoms. To extract meaningful features from interactions between the surface metal atoms and the $\mathrm{C}(111)$ substrate atoms, we restricted the relaxation of the left-side metals to the structures of Fig. 5.1, where the leftside metals were relaxed only along the surface-normal (z) direction with their lateral atomic positions fixed to those of Fig. 5.1. The geometry optimization was carried out until the remaining forces of the atoms were smaller than $0.02 \mathrm{eV} / \AA$.

For a more detailed analysis of the interactions of the metal atoms with diamond (111) surface, projected crystal orbital Hamilton population ( pCOHP ) analysis $[53,54]$, which is a partitioning scheme of the Kohn-Sham band-structure energy in the plane-wave DFT calculations in terms of orbital-pair contributions, was performed using the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) package [55]. The bond-analytical pCOHP provides quantitative information for bonding, nonbonding, and antibonding contributions in the plane-wave DFT calculations.


Figure 5.1 Top and side views of the transition metal terminated diamond (111) surfaces. (a) Diamond bulk-like $1 \times 1$ model and (b) Pandey chain $2 \times 1$ model. Large grey circles represent transition metal atoms (M), and small brown circles carbon atoms (Cn). Cn denotes the carbon atoms in the $n-t h$ carbon layer. The $(2 \times 1)$ surface unit cell is denoted by the black lines.

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### 5.3. Results

### 5.3.1. Interfacial Energies

To determine the relative stability between the $1 \times 1$ and $2 \times 1$ M/C (111) interfaces, we calculated the interfacial energy differences per surface $M$ atom of a $1 \times 1$ surface unit cell [ $\Delta E_{\text {int }}(\mathrm{eV} / 1 \times 1$ surface] between the two interfaces for each transition metal element as follows: $\Delta E_{\text {int }}=\left(E_{M / C(111)}^{2 \times 1}-E_{M / C(111)}^{1 \times 1}\right) / 2$. Here $E_{M / C(111)}^{2 \times 1}$ and $E_{M / C(111)}^{1 \times 1}$ are the total energies of the $2 \times 1$ and $1 \times 1 \mathrm{M} / \mathrm{C}(111)$ interfaces, respectively. Fig. 5.2 shows the interfacial energy differences $\Delta E_{\text {int }}$ between the $1 \times 1$ and $2 \times 1$ models of $\mathrm{M} / \mathrm{C}(111)$ in the form of a periodic table. Under this convention, a more positive value of $\Delta E_{\text {int }}$ represents a favorable formation of the $1 \times 1 \mathrm{M} / \mathrm{C}(111)$ structure.

In Fig. 5.2, the stable regions of the $1 \times 1$ and $2 \times 1 \mathrm{M} / \mathrm{C}(111)$ structures are represented by bluish and orangish colors, respectively. Looking at the overall trend, the $1 \times 1$ model is stable in the central row regions of the periodic table, while the $2 \times 1$ model is stable in the side edge regions. As we go from the side edges to the central regions, the $1 \times 1$ model becomes more stable as shown in a more bluish color. The $1 \times 1$ model is the most stable in the group 6 elements. As we go down the periodic table for each group, except for groups 4 and 10, the positive (negative) value of $\Delta E_{i n t}$ tends to be more positive (negative) and the difference between

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$\Delta E_{\text {int }}$ values in the center and the edge regions become bigger.
Looking at the details of the $\Delta E_{\text {int }}$ results, interfaces of conventional catalytic elements of groups 8, 9, and 10 (Fe, Co, Ni, $\mathrm{Ru}, \mathrm{Rh}, \mathrm{Pd}$, Os, Ir, and Pt) have a stable $1 \times 1$ structure with $\Delta E_{\text {int }}$ in an energy range of $0.26 \sim 0.60 \mathrm{eV} /(1 \times 1$ surface $)$. Central elements of groups 6 and 7 (Cr, Mn, Mo, Tc, W, and Re) also have a stable $1 \times 1$ interface structure with $\Delta E_{\text {int }}$ in an energy range of 0.47 $\sim 0.68 \mathrm{eV} /(1 \times 1$ surface $)$. Elements of groups 4 and 5 ( $\mathrm{Ti}, \mathrm{V}, \mathrm{Zr}$, $\mathrm{Nb}, \mathrm{Hf}$, and Ta ) have a stable $1 \times 1$ interface structure with $\Delta E_{\text {int }}$ in an energy range of $0.19 \sim 0.59 \mathrm{eV} / 1 \times 1$ surface. Elements of group 3 (Sc, Y) have a slightly stable $2 \times 1$ structure with $\Delta E_{\text {int }}$ of -0.02 and $-0.07 \mathrm{eV} /$ atom. In groups 11 and 12 , except for Cu , most elements have a stable $2 \times 1$ interface structure with $\Delta E_{\text {int }}$ in an energy range of $-0.47 \sim-0.05 \mathrm{eV} /$ atom. It is noted that these values are higher than the corresponding value of $-0.78 \mathrm{eV} /$ atom for clean $\mathrm{C}(111)$. Thus, a very weak catalytic effect is expected for these elements of groups 11 and $12 . \mathrm{Cu}$ is the only element that has a positive $\Delta E_{\text {int }}$ value in the groups. Cu has a smaller value of 0.16 $\mathrm{eV} /$ atom than those of the conventional catalytic elements. This indicates that Cu is expected to have a weak catalytic effect as compared with the conventional catalytic elements.

| 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |  |
| -0.02 | 0.22 | 0.49 | 0.53 | 0.47 | 0.44 | 0.42 | 0.30 | 0.16 | -0.05 | $0.61 \sim 1.00$ |
| Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | $0.26 \sim 0.50$ |
| -0.07 | 0.19 | 0.56 | 0.64 | 0.55 | 0.51 | 0.46 | 0.26 | -0.25 | -0.25 | $0.00 \sim 0.25$ |
|  | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | $\begin{aligned} & -0.19 \sim 0.00 \\ & -0.29 \sim-0.20 \end{aligned}$ |
|  | 0.25 | 0.59 | 0.68 | 0.63 | 0.60 | 0.55 | 0.36 | -0.47 | -0.35 | $-1.00 \sim-0.30$ |

Figure 5.2 Interfacial energy difference between the $1 \times 1$ and $2 \times 1$ model of $\mathrm{M} / \mathrm{C}(111)$ surface. Bluish regions are $1 \times 1$ model stable elements with a positive value. Orangish regions are $2 \times 1$ model stable elements with a negative value. Interfacial energy difference $\Delta E_{\text {int }}[\mathrm{eV} / 1 \times 1$ surface $]$ is defined by $\left(E_{M / C(111)}^{2 \times 1}-E_{M / C(111)}^{1 \times 1}\right) / 2$.

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### 5.3.2. Structures

Next, we investigated structural changes induced by the adsorption of metal atoms on $\mathrm{C}(111)$. In the previous chapters, it is shown that the surface Ni adsorption on $\mathrm{C}(111)$ favors the diamond bulk-like $1 \times 1$ interface structure. In the $1 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ structure, as compared with the $1 \times 1$ clean $\mathrm{C}(111)$, the $\mathrm{C} 2-\mathrm{C} 3$ bond length was shortened, and this inhibited the C1-C2 bilayer from exfoliating to the graphene. In the $2 \times 1 \mathrm{Ni} / \mathrm{C}(111)$ structure, as compared with the $2 \times 1$ clean $\mathrm{C}(111)$, the $\mathrm{C} 1-\mathrm{C} 1$ ' bond length was elongated by the Ni adsorption. Thus, the Ni -induced structural changes well explained the favorable formation of the $s p^{3}$-bonded subsurface carbon structure of the $1 \times 1$ model as well as the weakening of the $\pi$-bonded carbon in the Pandey chain structure of the $2 \times 1$ $\mathrm{Ni} / \mathrm{C}(111)$. Therefore, we analyzed the structural changes in terms of two important bond lengths: C2-C3 bond in the $1 \times 1$ model and C1 - C1' bond in the $2 \times 1$ model.

Fig. 5.3 (a) shows the calculated C2-C3 bond lengths in $1 \times 1$ M/C(111). As we go from the left to the right in each row of the periodic table, the C2-C3 bond length decreases and then increases. As compared with the elements in the side edge region of the periodic table, the bond length of elements in the central region is much shorter and closer to the bond length ( $1.54 \AA$ ) in the bulk diamond, and the group 7 elements have the closest structural values to the bulk diamond. As we go down the periodic table for each group, for the elements in the central region, the bond length becomes much
closer to the bulk diamond structure, while for the elements in groups $3-4$ and $11-12$, the bond length exhibits little or opposite changes, respectively.

In Fig. 5.3 (b), we can see the variation of the $\mathrm{C} 1-\mathrm{C} 1^{\prime}$ bond length in $2 \times 1 \mathrm{M} / \mathrm{C}(111)$. As we go from the left to the right in each row of the periodic table, the $\mathrm{C} 1-\mathrm{C} 1$ ' bond length increases and then decreases. As compared with the elements in the side edge region of the periodic table, the $\mathrm{C} 1-\mathrm{C} 1$ ' bond length for elements in the central region are more elongated from the $\mathrm{C} 1-\mathrm{C} 1^{\prime}$ bond length ( $1.44 \AA$ ) in the Pandey $\pi$-bonded chain structure of clean $2 \times 1 \mathrm{C}(111)$. As we go down the periodic table for each group, for the elements in the central region, the interfacial $\mathrm{C} 1-\mathrm{C} 1$ ' bond lengths are more elongated from the $\mathrm{C} 1-\mathrm{C} 1^{\prime}$ bond length in clean $2 \times 1 \mathrm{C}(111)$, while for the elements in groups 3 and $11-12$, the interfacial $\mathrm{C} 1-\mathrm{C} 1$ ' bond length is rather closer to that in clean $2 \times 1 \mathrm{C}(111)$, and for the elements in group 4 and 5 , the variation in the $\mathrm{C} 1-\mathrm{C} 1^{\prime}$ bond length is small.

These structural features are highly associated with the $\Delta E_{\text {int }}$ results for the elements in the periodic table. Our structural analysis clearly shows that the center region elements have more $s p^{3}$-like interfacial structures close to the diamond bulk-like structure, whereas the side edge region elements have more $s p^{2}-$ like interfacial structures close to clean $2 \times 1 \mathrm{C}(111)$. This agrees well with the results in $\Delta E_{\text {int }}$.


Figure 5.3 (a) C2-C3 bond length in the $1 \times 1 \mathrm{M} / \mathrm{C}(111)$ and (b) C1C1' bond length in $2 \times 1 \mathrm{M} / \mathrm{C}(111)$. (solid circle -3 d , dashed triangle - 4d, dotted square - 5d).

### 5.3.3. M-C cleavage energy

Next, we investigated the interaction between metal layers and carbon substrate. Fig. 5.4 (a) and (b) show the $\mathrm{M}-\mathrm{C}$ cleavage energy of the $1 \times 1$ and $2 \times 1$ models of the $\mathrm{M} / \mathrm{C}(111)$, respectively. The $\mathrm{M}-$ C cleavage energy, which is the energy necessary to cleavage the M overlayer from the $C$ (111) substrate, is defined as follows: $E_{M-C}=$ $\left[E_{M}^{\text {layer }}+E_{\text {frozen } C(111)}\right]-E_{M / C(111)}$. Here, $E_{M}^{\text {layer }}$ and $E_{\text {frozen } C(111)}$ are the total energies of the isolated M layer and the $\mathrm{C}(111)$ frozen to the geometry of $\mathrm{M} / \mathrm{C}(111)$, respectively.

The central elements have stronger $\mathrm{M}-\mathrm{C}$ cleavage energy so that they can gain energy by the $\mathrm{M}-\mathrm{C}$ bond formation, while the side edge elements have weaker M-C cleavage energy. As we go down the periodic table of each group, the $\mathrm{M}-\mathrm{C}$ cleavage energy becomes much stronger at the central region and weaker at the side edge region, and the difference in $E_{M-C}$ between central and side edge elements becomes larger. It is noted that the $1 \times 1$ model has overall stronger M-C interaction energy than the $2 \times 1$ model has [see Fig. 5.4 (a) and (b)]. It indicates that the $1 \times 1$ model has more energy gain from the $\mathrm{M}-\mathrm{C}$ bond formation than the $2 \times 1$ model has. The trend of the $\mathrm{M}-\mathrm{C}$ cleavage energy is very related to the structural changes of the subsurface C atoms because $\mathrm{M}-\mathrm{C}$ bond formation causes subsurface electron rearrangement and changes the subsurface structure [see Fig. 5.3 and Fig. 5.4]. This indicates that the much stronger the $\mathrm{M}-\mathrm{C}$ bond, the more stable the $s p^{3}$-like interfacial structure.

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(a)

(b)


Figure $5.4 \mathrm{M}-\mathrm{C}$ cleavage energy of the (a) $1 \times 1$ and (b) $2 \times 1$ model in M/C(111)

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### 5.3.5. Electronic structures

To obtain detailed physical insight into energetic and structural changes induced by the adsorption of M atoms on $\mathrm{C}(111)$, we performed an electronic investigation of the $\mathrm{M} / \mathrm{C}$ (111) surfaces.

We first analyze the interactions between the M layer and the underlying $\mathrm{C}(111)$ substrate by examining electronic structures of the isolated M layer frozen to the geometry of $\mathrm{M} / \mathrm{C}(111)$ and clean C(111). Fig. 5.5 (a) presents the calculated projected densities of states (PDOSs) of the $3 d_{z^{2}}$ bands of the M layers for the selected elements in 3d transition metals. The black horizontal line indicates the peak position of the $2 p_{z}$ band of surface C 1 atom of $1 \times 1$ clean $\mathrm{C}(111)$ at -4.70 eV with respect to the vacuum level. It is noted that the $3 d_{z^{2}}$ band moves down with respect to the vacuum level as we go from left to right of the periodic row. The peak position of the $3 d_{z^{2}}$ band is closest to the black horizontal line (the peak position of the $2 p_{z}$ band) for group 7 Mn . From the view of the perturbation [87], the stabilization in the interaction of two bands is proportional to the overlap between the two wavefunctions of these two bands and inversely proportional to the energy difference between the two bands before interaction as follows

$$
\Delta \mathrm{E}=\frac{\left|H_{i j}\right|^{2}}{E_{i}^{\circ}-E_{j}^{\circ}}
$$

because the overlap between $3 d_{z^{2}}$ and $2 p_{z}$ bands in each metal and

C (111) system is almost similar, the interaction between $3 d_{z^{2}}$ and $2 p_{z}$ bands is governed by the energy difference between the two bands before interaction. Therefore, the interaction between $3 d_{z^{2}}$ and $2 p_{z}$ states is strongest for group 7 Mn . In the $2 \times 1$ system [Fig. 5.5 (b)], the interactions of the metal $3 d_{z^{2}}$ states with both $\pi$ and $\pi^{*}$ peaks of $2 p_{z}$ band are important. The averaged position of the $\pi$ and $\pi^{*}$ peaks is located at -4.82 eV with respect to the vacuum level, and it is closest to the peak position of the $3 d_{z^{2}}$ band of the central elements, such as Mn. Thereby, it can be expected that the interaction between the $M$ layer and $2 \times 1 \mathrm{C}(111)$ would be strongest for the central elements as well. These results well explain that the $\mathrm{M}-\mathrm{C}$ cleavage energy is the largest for the central elements in the periodic rows.

In addition, the strength of the $\mathrm{M}-\mathrm{C}$ bond can be analyzed by calculating the pCOHP. Fig. 5.6 (a) and (b) show the calculated pCOHP of the $\mathrm{M}-\mathrm{C}$ bond of the $1 \times 1$ and the $2 \times 1$ models of the M/C (111), respectively. Here, the positive values of -pCOHP denote bonding states of the $\mathrm{M}-\mathrm{C}$ bond, whereas the negative values denote antibonding states of the $\mathrm{M}-\mathrm{C}$ bond. We see that electron occupation increases as we go from left to right of the periodic row. At group 3 Sc, only bonding states of the $\mathrm{M}-\mathrm{C}$ bond are partially occupied, and then more bonding states are occupied until we go to group 7 Mn . At group 7 Mn , bonding states are fully-occupied, while antibonding states are fully - unoccupied. After group 7 Mn , antibonding states of the $\mathrm{M}-\mathrm{C}$ bond are more occupied as we go to the right side of the periodic row. Thereby, the $\mathrm{M}-\mathrm{C}$ bond becomes strongest for the
central elements like group 7 Mn , where electrons are fully occupying the bonding states of the $\mathrm{M}-\mathrm{C}$ bond. In the $2 \times 1$ model [Fig. 5.6 (b)], it has an overall similar trend to the $1 \times 1$ model, but much weaker peak intensity than the $1 \times 1$ model. This behavior is in agreement with the feature in the $\mathrm{M}-\mathrm{C}$ cleavage energy of Fig. 5.4. This well explains the stronger $\mathrm{M}-\mathrm{C}$ bond formation in the $1 \times 1$ model rather than the $2 \times 1$ model.

To obtain insight into the charge rearrangement, we also performed a charge analysis using an isosurface plot of the electron density difference $\Delta \rho$ for the selected $M / C(111)$ surfaces: $\Delta \rho=$ $\rho_{M / C(111)}-\rho_{C(111)}-\rho_{M}$. Here, $\rho_{M / C(111)}$ is the electron density of $\mathrm{M} / \mathrm{C}(111), \rho_{C(111)}$ is the electron density of the frozen clean $\mathrm{C}(111)$ surface without the M layer, and $\rho_{M}$ is the electron density of the frozen M layer. Fig. 5.7 (a) and (b) show the isosurface plots of $\Delta \rho$ for the selected $\mathrm{M} / \mathrm{C}(111)$ surfaces with the $1 \times 1$ and the $2 \times 1$ models, respectively. We see a substantial rearrangement of electrons around surface atoms. In the $1 \times 1$ model [Fig 5.7 (a)], we can the significant accumulation of electrons in the region between the M atom and C 1 atom in $\mathrm{M} / \mathrm{C}(111)$. The adsorption of the M atom on $\mathrm{C}(111)$ removes the dangling bond of the C 1 atom and forms a covalent-like $\mathrm{M}-\mathrm{C} 1$ bond. Besides, electron accumulation occurs between the C2-C3 bond. Fig. 5.7(a) shows a greater electron accumulation in the region between the C2 and C3 atoms for the central elements (V, Mn, and Co), as compared with the side edge elements ( Sc and $\mathrm{Cu} \mathrm{)}$. that the C2-C3 bond length is more shortened in the central elements
as represented in Fig. 5.3 (a). In the $2 \times 1$ model [Fig. 5.7 (b)], M atoms are bonded obliquely with the surface C 1 atom on the surface and interact covalently with the C 1 atoms by accumulating electrons in the region between the M and C 1 atoms. Interestingly, electron depletion occurs from the region above the $\mathrm{C} 1-\mathrm{C} 1$ ' bond for the central elements (V, Mn, and Co), but does not occur for the side edge elements ( Sc and Cu ). This electron depletion shows that severe weakening of the $\pi$-bonds of C 1 atoms occurs mainly for the central elements as represented in Fig. 5.3(b).
(a)


Figure 5.5 Projected density of states (PDOS) for the $3 d_{z^{2}}$ atomic band of the $M$ layer frozen to the geometry of $M / C$ (111) with the (a) $1 \times 1$ and (b) $2 \times 1$ models. The panels in the last columns of (a) and (b) represent the $2 p_{z}$ band of geometry-optimized clean $\mathrm{C}(111)$ with the $1 \times 1$ and $2 \times 1$ models, respectively. The black horizontal lines in (a) and (b) indicate the peak position of the $2 p_{z}$ band of the C1 atom in $1 \times 1$ clean $C(111)$ slab at -4.70 eV and the averaged positions of the $\pi-$ and $\pi *$-state peaks of the C 1 atom in $2 \times 1$ clean $\mathrm{C}(111)$ at -4.82 eV , respectively. The energy zero is set at the vacuum energy.
(a)

(b)


Figure 5.6 Projected crystal orbital hamilton population (pCOHP) analysis for the $\mathrm{M}\left(3 d_{z^{2}}\right)-\mathrm{C}\left(2 p_{z}\right)$ bond of $\mathrm{M} / \mathrm{C}(111)$ with the (a) $1 \times 1$ and (b) $2 \times 1$ models. The horizontal line at the energy zero indicates the Fermi energy level of $\mathrm{M} / \mathrm{C}(111)$. The bonding states are indicated as a positive value of -pCOHP , while the antibonding states are indicated as a negative value.

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(a)

(b)


Figure 5.7 Isosurface plots of electron density difference $\Delta \rho$ with the top and side views of the $M / C$ (111) surfaces with the (a) $1 \times 1$ and (b) $2 \times 1$ models. Electron accumulation and depletion regions are denoted by yellow and blue, respectively. The isosurface levels are $\pm 0.007$ electrons/bohr3.

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### 5.3.5. Carbide formation

As another perspective reactive factor when selecting a catalytic metal for $\mathrm{M} / \mathrm{C}(111)$, we consider the tendency of MC carbide formation. It is well known that, as we go to the left of the periodic rows, MC carbide formation energies become lower as compared with the other elements of the periodic rows and thereby MC carbide formation becomes favorable [88, 89]. Such formation of these metal carbides would prevent metal elements from forming M films on C(111) and being powerful diamond catalysts since much higher temperatures and pressures are required to dissolve these carbides. To determine the relative stability of the formation of $\mathrm{M} / \mathrm{C}(111)$ concerning the formation of MC carbides, we calculated the relative film formation energy $\Delta E_{f}$ of metal M per a $1 \times 1$ surface unit cell for $1 \times 1 \mathrm{M} / \mathrm{C}(111)$ as follows: $\Delta E_{f}=\left[E_{M / C(111)}-\left(\mu_{M}+E_{C(111)}\right)\right] / 2$. Here, $\mu_{M}$ is the chemical potential of the M atom in the MC carbide ( $\mu_{M}=$ $E_{M C}-\mu_{C}$, where $\mu_{C}$ is the chemical potential of the carbon atom in the bulk graphite). The MC carbide has a rock-salt structure and its lattice constant was fully optimized. Fig. 5.8 shows the film formation energy $\Delta E_{f}$ of metal M for $1 \times 1 \mathrm{M} / \mathrm{C}(111)$ concerning the formation of rock - salt MC carbides. We see that, before 6 , the formation of MC carbides is more favorable than the formation of $1 \times 1 \mathrm{M} / \mathrm{C}(111)$. Thus, early transition metals in groups 3, 4, 5, and 6 have a low tendency to form M/C (111) for the catalytic effect, as compared with groups 7, 8, 9, and 10 .


Figure 5.8 Film formation energy $\Delta E_{f}$ of metal $M$ per a $1 \times 1$ surface unit cell for $1 \times 1 \mathrm{M} / \mathrm{C}$ (111) with respect to the formation of rock-salt MC carbides. The positive values of $\Delta E_{f}$ represent the favorable formation of $M C$ carbides, while the negative values represent the favorable formation of M films on $\mathrm{C}(111)$ with the structures of $1 \times 1 \mathrm{M} / \mathrm{C}(111)$.

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### 5.4. Discussion

DFT calculations were used to analyze the interfacial structures of $M / C(111)$. It was found that the central elements (groups $4,5,6$, $7,8,9$, and 10) favor the stable $s p^{3}$-like $1 \times 1$ interfacial structure, while the side edge elements (groups 3, 11, and 12) favor the $s p^{2}-$ like $2 \times 1$ interfacial structure. Further film formation energy calculations for carbide formation showed that the early transition metals (groups $3,4,5$, and 6 ) are easy to form the MC carbide rather than the M layer on $\mathrm{C}(111)$ for the catalytic effect.

So far, melting temperatures $\mathrm{T}_{\mathrm{m}}$ for metals M are considered to play a crucial role as a key factor for catalytic diamond synthesis [22]. $\mathrm{T}_{\mathrm{m}}$, however, doesn't clearly explain why Cu plays a role as a catalyst, while Ag and Au do not despite similar $\mathrm{T}_{\mathrm{m}}$ to that of Cu [24]. Therefore, to better analyze the catalytic effect of metals, we introduce another parameter $\Delta E_{\text {int }}$, between the $1 \times 1$ and $2 \times 1$ models of M/C(111). Firstly, we consider the elements of groups 11 and 12 in the lower left area of Fig. 5.9. These elements have lower $\mathrm{T}_{\mathrm{m}}$ and $\Delta E_{\text {int }}$ values than the others have. Despite their lower $\mathrm{T}_{\mathrm{m}}$, these elements show a worse catalytic efficiency because of lower $\Delta E_{\text {int }}$ as compared with the other transition metals. It is noted that, among groups 11 and $12, \mathrm{Cu}$ has the highest $\Delta E_{\text {int }}$ value. This well explains experiments conducted by Kanda et al. for $\mathrm{Cu}, \mathrm{Zn}$, and Au in 1994, where Cu showed the best catalytic efficiency [24]. They also observed that Cu exhibited catalytic effect at a much higher

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temperature than its $\mathrm{T}_{\mathrm{m}}$, and this behavior is different from conventional catalysts that do a catalytic effect in the liquid phase around their $\mathrm{T}_{\mathrm{m}}$. So, they called the temperature "the reaction temperature". We think that "the reaction temperature" is associated with $\Delta E_{i n t}$ we propose in this study for surface catalytic effects. Therefore, it is important to consider $\Delta E_{i n t}$ in addition to $\mathrm{T}_{\mathrm{m}}$ that has been considered so far as a key factor for catalytic diamond synthesis.

Secondly, we consider the elements of groups 7, 8, 9, and 10 in the upper - right area of Fig. 5.9. Overall, They have relatively higher $\mathrm{T}_{\mathrm{m}}$ and higher $\Delta E_{\text {int }}$ values than the elements of groups 11 and 12 do. Most of these elements are the conventional catalytic elements identified by G.E. in 1955 when they first developed synthetic diamonds [21, 22]. It is noted that, among these elements, Fe, Co, Ni, and Mn (red circled area in Fig. 5.9.) have the lowest $\mathrm{T}_{\mathrm{m}}$. Even today, these are the most powerful catalytic metal elements. More detailed experimental results for these four catalysts showed that Mn, Fe, Co, and Ni have growth temperatures lowering in this order, although they have similar $\mathrm{T}_{\mathrm{m}}[22,89,90]$. Interestingly, in our calculation, Mn, Fe, Co, and Ni have $\mathrm{M}-\mathrm{C}$ cleavage energies lowering in this order [Fig. 5.4(a)]. In the previous chapters, we suggested surfactantmediated growth in the $\mathrm{Ni} / \mathrm{C}(111)$ system, in which Ni atoms exchange their positions with incoming C atoms for continuous diamond growth, maintaining the $1 \times 1 \mathrm{M} / \mathrm{C}(111)$ structure. In this process, the $\mathrm{M}-\mathrm{C}$ bonds must be cleaved and instead, the $\mathrm{C}-\mathrm{C}$ bond is newly formed. Thus, the moderate $\mathrm{M}-\mathrm{C}$ bond strength would be important for diamond synthesis because that is advantageous to
kinetics for continuous diamond growth in $\mathrm{M} / \mathrm{C}(111)$.
Lastly, the elements of groups 3, 4, 5, and 6 are seen in the upper-right area of Fig. 9. Although these elements have similar $\mathrm{T}_{\mathrm{m}}$ and $\Delta E_{\text {int }}$ values to the elements of groups $7,8,9$, and 10 , these elements tend to form metal carbides rather than $\mathrm{M} / \mathrm{C}(111)$. The formation of metal carbides would prevent the metal elements from forming M films on $\mathrm{C}(111)$ and being powerful diamond catalysts. This result coincides with the experimental results of Wakatsuki that the elements of groups $3,4,5$, and 6 exhibited no catalytic behavior below $2000{ }^{\circ} \mathrm{C}$ [83].


Figure 5.9 Scatter plot of two parameters for metals M: Experimental melting temperature ( Tm ) of metals M and the interfacial energy difference ( $\Delta E_{\text {int }}$ ) between $1 \times 1$ and $2 \times 1 \mathrm{M} / \mathrm{C}(111)$. Experimental Tm data are taken from Ref [89]. The black circles indicate elements in groups $3,4,5$, and 6 , the green circles indicate elements in groups $7,8,9$, and 10 , and the violet circles indicate elements in groups 11 and 12 . The same colored dotted curves indicate the regions of these groups.

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### 5.5. Conclusion

Using density functional theory, we calculated interfacial energy difference $\Delta E_{\text {int }}$ between the $1 \times 1$ and $2 \times 1$ models of transition metal (M) on C(111) [M/C(111)] surfaces, which are very important in understanding the catalytic effect of transition metals in the growth of diamond on $\mathrm{C}(111)$. The calculation results suggest that the central elements (groups 4, 5, 6, 7, 8, 9, and 10) favor the stable $1 \times 1 \mathrm{M} / \mathrm{C}(111)$ structure with the diamond bulk-like structure at the interface, while the side edge elements (groups 3, 11, and 12) favor the $2 \times 1 \mathrm{M} / \mathrm{C}(111)$ structure with $2 \times 1$ Pandey chain model of $C(111)$. For a detailed understanding of the interaction between the $M$ layer and the $\mathrm{C}(111)$ substrate, the analysis of the atomic structures, the $\mathrm{M}-\mathrm{C}$ cleavage energies, and the electronic features was also performed. Further calculations of film formation of metal carbides showed that the early transition metals (groups 3, 4, 5, and 6) tend to form metal carbides rather than M/C(111). This behavior prevents the metal elements in groups $3,4,5$, and 6 from forming the $M$ film on $C(111)$ and acting as a powerful catalyst for diamond growth. Based on our calculations of $M / C(111)$ with the $1 \times 1$ and $2 \times 1$ models, we herein proposed another parameter $\Delta E_{i n t}$ representing surface catalytic effect in addition to carbon solubility and $\mathrm{T}_{\mathrm{m}}$ of metals that have been considered in the diamond synthesis. The atomic model used here can also be applied to other elements and alloys that will be used for diamond synthesis in the future.

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# Chapter 6. Catalytic effect of excess charges on the diamond (111) surface 

### 6.1. Introduction

Introducing the gas activation system, such as Hot Wire Chemical Deposition (HWCVD) [28] or Plasma Enhanced Chemical Vapor Deposition (PECVD) [27], diamond synthesis promoted because these gas activation systems provided a synthetic method with the high-quality and high-growth rate of crystalline diamond thin films through the high charge density in a vacuum chamber. Several pieces of research [29, 30, 33] have suggested that the interaction of charges with the diamond in the vacuum chamber is important and requires a microscopic view of the interaction of them on the surface or grain boundaries. Recently, it has been shown that grain boundary charging produced by electric-pulsing is an additional driving force to promote recrystallization, whose mechanism and chemistry are associated with the bond softening on grain boundary core that is observed in ab-initio phonon calculation [91]. Thus, surfaces of the diamond can be an active site for the interaction with charges in the thin film growth. It is well known that the Pandey chain structure [38, 39] of diamond $C$ (111) reconstructs from its $2 \times 1$ stable $\pi$-bonded surface structure into a $1 \times 1$ diamond-like structure by adsorption
of hydrogen and fluorine [59, 86]. Introducing a charge, which interacts with hydrogenated $C$ (111) surface, and hence changing the surface structure, will be a new field of study in diamond growth.

Interesting results obtained from several previous theoretical studies attracted further interest in the charging effect on the diamond surface. Lai et al. [92] reported that negatively charged diamond nanoparticles can reconstruct their $\pi$-bonded surface structure, whereby the surface structure only has $s p^{3}$-character after removal of surface-most $\pi$-bonded layer. This interesting result leading to the thermodynamically stable formation of $1 \times 1$ surface structure is interpreted as the charging effect of the diamond surface. In another work by Lai [93], they reported that the hydrogenated and un-hydrogenated surfaces of diamond nanoparticles can be changed reversibly by charging, which in turn storage hydrogens on the surface depending on the charge state of the system. These results point out the crucial feature: modification of the surface structure of diamond by negatively charging will be stabilizing the $s p^{3}$ structure, and positive charging will be stabilizing the $s p^{2}$ structure.

It is observed experimentally that diamond nanoparticles formed in the vacuum chamber are negatively charged, and this diamond nanoparticle can be the source of high-quality and high-growth rate diamond thin films through applied electric bias [31]. Atomic hydrogen is chemisorbed to a bare diamond surface with strong binding energy. In the negative charging system, the excess electrons can dissociate the $\mathrm{C}-\mathrm{H}$ bond and its active sites like
dangling bonds can be occupied by excess electrons remaining the $1 \times 1$ surface structures [94, 95]. In contrast to negative charging, the positive charging of diamond surface is rather destructive on $1 \times 1$ structure and favors the formation of graphite. The crucial questions to be addressed are how negative charging of the diamond C(111) surface can strongly influence to favorable formation of the high-quality diamond surface structures and why positive charging prevents diamond formation.

The purpose of this chapter is to understand the charging effect on the diamond surface through the theoretical quantum calculation. We carried out calculations for charged diamond C(111) slab with
 the negative charging or by removing electrons for the positive charging to total system charges. This study also suggests a limitation of the plane wave (PW) for the charged system using PBC and suggests local atomic orbital (AO) basis sets in the ab-initio calculations of charged systems using PBC. We investigated the intrinsic problem of the plane-wave basis set method, such as outspilling and in-spilling of charges that were reported in charged PBC systems [96, 97].

### 6.2. Computational Details

We performed spin-unpolarized density function theory (DFT) calculations using the projector-augmented wave method [51]. For
the exchange-correlation functional, we used generalized gradient approximation using Perdew, Burke, and Ernzerhof (PBE) [50]. The two different ab-initio simulation packages, VASP [49] and SIESTA [98], are used to compare the two different basis sets, plane waves (PW) and local atomic basis (AO) sets, respectively.

In PW calculations, plane waves having kinetic energies until 400 eV is used for the basis set. self-consistent electronic calculations are performed until the energy convergence of $10^{-6} \mathrm{eV}$ is achieved and atomic positions are optimized by the conjugate gradient method until atomic forces are minimized below $0.02 \mathrm{eV} / \AA$. In AO calculations, we used linear combinations of numerical atomic orbitals for the basis set to express eigenfunctions of the Kohn-Sham Hamiltonian. We chose a 200 Ry mesh cutoff and the self - consistent calculations are performed until the convergence criterion for the density matrix differences of $10^{-4}$ is achieved with a mixing ratio of 0.05 . Core regions of electrons are expressed by norm-conserving nonlocal Trouiller-Martins pseudopotentials [99].

### 6.3. Results and Discussion

### 6.3.1. Comparison of PW and AO methods

Before we investigate charging effects on the hydrogenated diamond $C$ (111) surface, we first examine the limitation of the PW calculation within periodic boundary condition ( PBC ), in which the

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diamond slab and vacuum spacing are repeated periodically along the $z$-axis. The cell is made up of $(2 \times 2)$ unit plane of diamond with 12 layers [Fig. 6.1]. In the charged system within PBC , the total energy of the system has divergent total energy because of infinitely repeating excess charges in neighboring cells and additional background charges of opposite polarity are needed to neutralize cells and hence to achieve the convergence of total energy [100, 101]. Despite the neutral background charging correction, calculations of the charged system within PBC are strongly dependent on vacuum spacing than the neutral system because of electrostatic interactions between charges of neighboring cells. Therefore, we always need a cell with a vacuum space large enough to ignore the electrostatic interactions between the charges of the neighboring cells. However, PW calculation in a large vacuum cell has a fatal drawback as the following results.

In Fig. 6.2, we present the plane-averaged total potential energies [dashed curves] and excess charges [solid curves] of the negatively charged system (addition of $1 \mathrm{e} / \mathrm{unit}$ cell) along the $z^{-}$ direction with increasing vacuum distances of 5,10 , and $20 \AA$. The total potential energy includes self-consistent electronic potential and exchange-correlation potential. The excess charges are computed by the difference between the charged cell and neutral cell frozen to the geometry of the charged cell. The diamond slab with 12 layers is symmetrically located in the center of the cell, and both sides of them are occupied by the same vacuum spacing. Dashed vertical lines indicate the atomic positions of each carbon layer and a

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dashed horizontal line indicates the Fermi energy level of each supercell system. The total potential (dashed curves) repeats periodically inside the cell, then reaches its maximum at the surface.

In Fig. 6.2(b), we can see the enlarged part of Fig. 6.2(a) indicated by the red square. In the vacuum region, as the vacuum distance increases, the potential curve goes further down, and in the $20 \AA$ system, it goes below the Fermi level and generates a quantum well in the vacuum region. Normally, tunneling can happen if the electrons can tunnel the surface tunneling barrier. However, the PW calculation within PBC always acquires solutions in this quantum well and electrons spill out into the vacuum region. We can see the excess charge density spilled out into the vacuum region in the case of $20 \AA$ vacuum distance [see blue dashed line in Fig. 6.2(b)]. As the vacuum distance increases, this quantum well region becomes wider and deeper, and thus the amount of charge escaping the surface increases further. This out-spilling of excess electrons is an artifact in the calculations with PW basis set and PBC.

On the other hand, in a small vacuum system like $10 \AA$ case, there is no out-spilling into the vacuum and we may acquire reasonable results. However, we have to be careful that the charge can spill inwards by the electrostatic forces from the charges of the neighboring cells. In Fig. 6.2(c), we can see potentials and excess charge density in the subsurface and bulk region, which is an enlarged plot from the green area in Fig. 6.2 (a). As the vacuum size decreases, more excess charges accumulate in the subsurface and bulk regions. This may also be another artifact if it is not the desired result. And
in a very small vacuum system like $5 \AA$ case, the excess charge ends discontinuously at the end of the supercell [Fig. 6.2(b) red dashed line], which means that it is directly connected to the next cell and is an obvious artifact.

Fig. 6.3 shows the AO calculation results with the same diamond slab structures as Fig. 6.2 using the SIESTA package. Although the potential curves go down below the Fermi energy level as the vacuum distance increases, we cannot observe any out-spilling in the vacuum region, because the AO basis set only support the electronic states around atomic sites, not in the vacuum region. Therefore, we can calculate the converged results that minimize the interaction with the adjacent cell using the AO basis set. The vacuum energy level with respect to Fermi level and bond lengths as the vacuum size is increased is shown in Fig. 6.4 and Fig 6.5.

Although a problem of out-spilling was found in the negative charging calculation using the PW basis set, there was no problem in the positive charging calculation. The reason is that, in a positive charging case, the potential well is not created in the vacuum region because it has a positive slope of potential in vacuum [not shown here]. Therefore, the calculation of increasing the vacuum size will also have no problem with the PW basis.


Figure 6.1 Side views of the H -terminated $\mathrm{C}(111)$ surfaces. The $1 \times 1$ model: (a) $0 \%$, (b) $25 \%$, (c) $50 \%$, (d) $75 \%$, and (e) $100 \%$. The $2 \times 1$ model: (f) $0 \%$, (g) $25 \%$, (h) $50 \%$, (i) $75 \%$, and (j) $100 \%$. White and brown spheres represent H and C atoms, respectively.

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Figure 6.2 (a) 'The plane-averaged potential and excess charge density of negatively charged (1 e/unitcell) 12 layers of diamond $C$ (111) clean surface with $1 \times 1$ model located at the center of supercell. The different vacuum spacings are denoted by different colors of red ( $5 \AA$ ), green ( $10 \AA$ ), and blue ( $20 \AA$ ), respectively. The horizontal dashed black line indicates the Fermi energy level and the vertical dashed black lines indicate the positions of each atomic layer. (b) The enlarged picture of the red square area in the plot (a). (c) The enlarged picture of the green square area in the plot (a).
(a)

(b)


Figure 6.3 The plane-averaged (a) excess charge density and (b) potential energy of negatively charged (1 e/unitcell) diamond (111) bare surface located at the center of supercell. The vacuum spacings between two adjacent diamond slabs are denoted by different colors of cyan ( $5 \AA$ ), red ( $10 \AA$ ), green (20 $\AA$ ), blue ( $40 \AA$ ), yellow ( $80 \AA$ ), pink (160 $\AA$ ), orange (320 $\AA$ ), and black ( $640 \AA$ ), respectively. The horizontal dashed black lines in the potential curve represent the Fermi energy level and the vertical dashed black lines in both plots represent the position of each layer atoms.

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Figure 6.4 The relative position of vacuum level with respect to the Fermi level with increasing vacuum spacing.


Figure 6.5 The bond length of negatively charged ( 1 e/unitcell) $1 \times 1$ clean $\mathrm{C}(111)$ with respect to the vacuum spacing; (a) $\mathrm{C} 1-\mathrm{C} 2$ bond and (b) C2-C3 bond.

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### 6.3.2 Large vacuum spacing - AO calculation

Having discussed the limitation of PW basis sets in representing charged diamond using PBC in large vacuum spacing, we explore the calculated AO results charged situation for the diamond bare surface with large vacuum spacing of $640 \AA$. When it is neutral, the topmost C1 atom layer is relaxed inward and the C2-C3 bond length is elongated so that C1 and C2 layer form graphite-like thin double layer. The AO calculation yields that the Pandey chain $2 \times 1$ structure is energetically the most favorable surface structure in clean $1 \times 1 \mathrm{C}(111)$ for the neutral case.

Fig 6.6 (a) shows the hydrogen effect on charge-neutral diamond $\mathrm{C}(111)$ surfaces with increasing hydrogen coverage. The calculated surface energy, $\Delta E_{\text {surf }}$, is defined as the energy difference between the $1 \times 1$ and $2 \times 1$ model of $H / C(111)$ as follows: $\Delta E_{\text {surf }}=$ $\left(E_{1 \times 1}-E_{2 \times 1}\right) / 2$. The hydrogen coverage increasing and the stabilization of the $s p^{3}$-like structure with the $1 \times 1$ model are interrelated. As the adsorption of hydrogen is increased, the $\Delta E_{\text {surf }}$ is reduced from $0.78 \mathrm{eV} /(1 \times 1$ surface $)$ to $-0.61 \mathrm{eV} /(1 \times 1$ surface $)$ in the neutral case. Thus, above $50 \%$ of hydrogen coverage, it is more favorable to form the $s p^{3}$ like $1 \times 1$ surface structure than $2 \times 1$ surface structure.

When the negatively charging is applied to the optimized neutral $C$ (111) surface, the negative charges induce an additional energy change. Fig. 6.6 (b) shows the additional energy change induced by negatively charging the neutral C (111) surface. It is calculated as the
difference of $\Delta E_{\text {surf }}$ values between $\Delta E_{\text {surf }}$ at maximal charge density and $\Delta E_{\text {surf }}$ at neutral. The maximal charge density is defined as the energy density when $E_{\text {vacuum }}-E_{\text {fermi }}=0$. The maximal charge density of $H / C(111)$ surfaces according to each hydrogen coverage is shown in Fig. 6.6 (c). In Fig. 6.6 (b), we can see that the negatively charged clean $C(111)$ surface has an additional positive energy change, which means the $1 \times 1$ structure is relatively more unstable by negative charging. As the hydrogen coverage is increased, the direction of an additional energy change is reversed to a negative value, which means the $1 \times 1$ structure is relatively less unstable or more stable by negative charging with respect to the neutral case. This additional energy change by negative charging has the highest value in the $25 \%$ and $50 \%$ hydrogen coverage and it is reduced in $75 \%$ and $100 \%$ hydrogen coverage. The highest energy change is -0.016 $\mathrm{eV} /(1 \times 1$ surface $)$ at $25 \%$ hydrogen coverage. However, an amount of energy change by negative charging is very small compared with hydrogen effects in neutral cases. Comparing Fig. 6.6 (a) and (b), the energy scale of the charging effect is an order smaller than that of the hydrogen effect. The arrows in the plot Fig. 6.6(a) indicate the direction and magnitude of excess charge effects on each hydrogen coverage.

Fig. 6.7 shows the bond length change induced by negative charging of the neutral clean and H -terminated surfaces with increasing hydrogen coverage. Fig. 6.7 (a) shows the $\mathrm{C} 1-\mathrm{C} 2$ bond and C2-C3 bond length of $1 \times 1 \mathrm{C}(111)$ surfaces. The $\mathrm{C} 1-\mathrm{C} 2$ bond length is increased by the negative charging at $0 \%$ hydrogen
coverage, and an amount of length change is reduced as we go to the case of the high hydrogen coverage. The C2-C3 bond length, which is important to determine the proportion of $s p^{3}$-bond stabilization of the $C$ (111) surface, remains relatively unchanged compared with the C1-C2 bond. Fig. 6.8(b) shows the bond length change of the $\mathrm{C} 1-$ C 2 and $\mathrm{C} 1-\mathrm{C} 1$ ' bonds. It also shows that the $\mathrm{C} 1-\mathrm{C} 2$ bond is elongated by the negative charging at $0 \%$ hydrogen coverage and then an amount of length change decreases as hydrogen coverage increases. The bond length change of the C1-C1' bond, which is an indicator of $\pi$-bond weakening of $2 \times 1 \mathrm{C}(111)$, is very small and relatively remains unchanged. Thus, the main effect of negative charging on both $1 \times 1$ and $2 \times 1 \mathrm{C}(111)$ surface is the elongation of the C1-C2 bond. Small changes in two important bond lengths, which are the $\mathrm{C} 2-\mathrm{C} 3$ bond of $1 \times 1$ model and $\mathrm{C} 1-\mathrm{C} 1^{\prime}$ bond of $2 \times 1$ model, well explains why the energy change induced by negative charging is relatively small on the $C$ (111) surface.

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Figure 6.6 Calculated results with the hydrogen coverage. The surface energy difference, $\Delta E_{\text {surf }}[\mathrm{eV} / 1 \times 1$ surface], is defined as the difference of the total energy of the $\mathrm{C}(111)$ between $1 \times 1$ and $2 \times 1$ models as follows: $\Delta E_{\text {surf }}=\left(E_{1 \times 1}-E_{2 \times 1}\right) / 2$. (a) $\Delta E_{\text {surf }}$ of neutral $\mathrm{H} / \mathrm{C}(111)$. (b) $\Delta E_{\text {surf }}$ of charged $\mathrm{H} / \mathrm{C}(111)$ with respect to neutral $\mathrm{H} / \mathrm{C}$ (111). (c) The maximal charge density [e $/ 1 \times 1$ surface] that is defined as the charge density when $E_{\text {vacuum }}-E_{\text {fermi }}=0$. The arrows in plot (a) indicate the direction and magnitude of excess charge effects on each hydrogen coverage.


Figure 6.7 The bond length change induced by negative charging on clean and hydrogenated C (111) surfaces with the (a) $1 \times 1$ model and (b) $2 \times 1$ model.

### 6.3.3. Small vacuum spacing - PW calculation

In the previous section, we found that, at a large vacuum system, most charges are on the outside the surface due to reduced external electrostatic force from neighbor cells. As a result, the charge density in the subsurface is relatively low, and the charging effect on subsurface atoms is reduced. This deficient charge density in the inner subsurface region was the main reason for small structural change and following small energy changes. In the reality, a gasactivation system like HWCVD generates $10^{17}$ electrons/s/cm2 and has high electron density in vacuum spacing. The high charge density in a vacuum could be an electrostatic force to promote the charging of the subsurface region of the negatively charged slab. In other words, the degree of charging of the surface may be related to the charge density in the vacuum. In this respect, we should consider again the behavior of charging in a small vacuum spacing system in which electrostatic force promotes the subsurface charging by high vacuum charge density.

Although PW calculations have an artifact of out-spilling of excess negatively charging in large vacuum spacing, the calculation in small vacuum spacing has no problem in spilling of charges into the vacuum space. Also, unlike AO calculations, PW calculations do not have the problem of completeness of the basis set, and can systemically optimize the magnitude of basis-sets. Therefore, in this section, we will show the result of PW calculation using VASP for a clean $1 \times 1 \mathrm{C}(111)$ surface with small vacuum spacing $10 \AA$. Fig.

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6.8 (a) and (b) show the calculated plane-averaged excess charge density and potential energy along the $z$-axis, respectively. Black and green colored lines mean the negatively charged (electron addition by 1.0) and positively charged (electron removal by -1.0 ) case of the $C(111)$ surface, respectively. Red lines mean the other cases having excess electrons range from 0.9 to -0.9 with an increment of $0.1|\mathrm{e}|$. The horizontal dashed lines in the potential curve [Fig. 6.8(b)] represents the Fermi energy level and the vertical dashed lines [Fig. 6.8 (a) and (b)] represent the position of each layer of atoms. There is no quantum well-like electron confinement in the vacuum region, which is in contrast with the results by PW calculations with high vacuum spacing of $20 \AA$. Fig. As the amount of excess electrons increases, the vacuum line of the potential curve gradually falls closer to the Fermi level. Therefore, adding more excess electrons will cause out-spilling as in high vacuum spacing. Fig. 6.8 (c) shows the bond length change by positive and negative charging on clean $1 \times 1 \mathrm{C}(111)$ surfaces with an excess electron range from -1.0 to 1.0. Interestingly, as the amount of excess electrons increases, the $\mathrm{C} 1-\mathrm{C} 2$ bond length increases, and the C2-C3 bond length decreases. When it is positively charged, the $\mathrm{C} 1-\mathrm{C} 2$ bond length decreases, and the C2-C3 bond length increases. Therefore, the structure of the surface changes to a $s p^{3}$-like structure by negative charging and a $s p^{2}$-like structure by positive charging. These results are contrasted with those of high vacuum spacing case in the previous section, which showed little effect in C2-C3 bond length and energy, and these results are similar to the
previously reported calculation results of several charged C(111) systems. Therefore, it is highly likely that the charge effects were related to the small vacuum spacing system.


Figure 6.8 Calculated results in PW method using VASP with a small vacuum (10 $\AA$ ). (a) The plane-averaged excess charge density and (b) Potentials of the clean $1 \times 1 \mathrm{C}(111)$ surface with various charged states. Black and green colored lines mean the negatively charged (1 e/unitcell) and positively charged ( -1 e eunitcell) case of the C(111) surface, respectively. Red lines mean the cases having excess electrons range from 0.9 to -0.9 with an increment of 0.1 e . (c) The bond length change by negative charging on clean $1 \times 1 \mathrm{C}(111)$ surfaces with excess electron range from -1.0 to 1.0.

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### 6.4. Conclusion

To understand the charging effect on the diamond surface, we investigated charged clean and hydrogenated C(111) surface and we also discussed the limitations and artifacts of the plane-wave (PW) basis set within periodic boundary conditions (PBC) in calculating the charged systems. While PW methods have no problem in calculating the neutral and positively charged system, PW methods create the spurious out-spilling of excess charges in the large vacuum spacing in the negatively charged systems. but it is appropriate to calculate the small charged system with small vacuum spacing. Our analyses are expected to be helpful for future calculations of excess charged systems.

Through the AO calculation, we were able to optimize the geometry by increasing the vacuum and obtain the result converged in the large vacuum cell. We found that the bond $\mathrm{C} 1-\mathrm{C} 2$ bond length is elongated with negative charging. However, two important bond lengths, the $\mathrm{C} 2-\mathrm{C} 3$ bond in the $1 \times 1$ model and the $\mathrm{C} 1-\mathrm{C} 1^{\prime}$ bond in the $2 \times 1$ model remain unchanged by negative charging. This is because, as the vacuum size increases, the electrostatic force from the neighboring cell decreases and all of the charges go to the surface, thereby reducing the internal subsurface charge density. The maximum charging amount is calculated as -0.015 [e/ $1 \times 1$ surface] in $1 \times 1 \mathrm{H} / \mathrm{C}(111)$ with $75 \% \mathrm{H}$-coverage and $-0.012 \quad[\mathrm{e} / 1 \times 1$ surface] in $2 \times 1 \mathrm{H} / \mathrm{C}$ (111) with $75 \%$ coverage. Considering the high
charge density of the vacuum in the real experiment, this charging amount is very small and we may consider the situation that more electrons enter into the surface to observe charging effects. For this purpose, we carefully investigated calculations in a small vacuum cell with PW calculations, and we found that the $\mathrm{C} 2-\mathrm{C} 3$ bond length decreased in negative charging and increased in positive charging, resulting in that negative charging promotes $s p^{3}$ and positive charging promotes $s p^{2}$. Thus, charging effects on diamond (111) surface are only observed in the small vacuum system that promotes charge accumulation in the subsurface region to influence the $\mathrm{C} 2-\mathrm{C} 3$ bond. These results may be related to the fact that we can observe the charging effects on diamond only in the HWCVD system having a high density of charge in the vacuum, not in other macro world having no high charge density in the vacuum.

## Chapter 7. Total Conclusion

Among the diamond low index surfaces, the $C$ (111) surface, which is commonly observed in the actual process, has a very stable surface $\pi$-bond called a Pandey chain. In the diamond growth process, it is necessary to remove the $\pi$-bond from the surface for continuous diamond growth. For this reason, extreme conditions of 130 kbar and 3000 K are required in the HPHT process without catalytic metals. If catalytic metal is used, this temperature and pressure can be reduced very much. However, the microscopic mechanism of catalytic metals has not been clearly understood yet. Similarly, in the CVD process, Pandey chains on the surface were also observed, which promoted the formation of graphite, requiring a cyclic process. To solve this problem, gas-activation techniques such as HWCVD were used, but the role and mechanism of the large amount of charge generated here have not yet been clearly identified. In this study, we investigated these two catalytic phenomena and we found the important common fact on the diamond surface. We firstly investigated the catalytic effect of transition metals in the HPHT system (chapters 3, 4, and 5), and then the catalytic effect of excess charges in the HWCVD system (chapter 6) using ab-initio calculations based on density functional theory (DFT).

First, we studied how the Ni catalytic metal affects the C(111) surface. Ni metal adsorbed onto $2 \times 1 \mathrm{C}(111)$ forming an $\mathrm{M}-\mathrm{C}$ covalent-like bond, thereby weakening the $\mathrm{C} 1-\mathrm{C} 1$ ' $\pi$-bond

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corresponding to the Pandey chain in $2 \times 1$ interfacial structure and energetically more stabilizing the $1 \times 1$ interfacial structure with the $s p^{3}$-bond than $2 \times 1$ interfacial structure with the $s p^{2}$-bond. It was also found that the stability of the $1 \times 1$ interfacial structure was related to the shortening of the C2-C3 bond length of the $1 \times 1$ model. This is expected to promote diamond nucleation by promoting the formation of a $s p^{3}-$ like interfacial structure by Ni catalysts. According to the subsequent $\mathrm{CI}-\mathrm{NEB}$ calculation, it was also revealed that Ni acts as a surfactant and allows the diamond to grow continuously through an exchange reaction with the supplied carbon atoms.

Additional Phonon calculations were performed to confirm the new role of Ni on the diamond surface experimentally in the future. Ni -terminated $\mathrm{C}(111)$ formed a Ni -localized phonon band at less than $300 \mathrm{~cm}^{-1}$, and a surface C -localized phonon band at $300-1400$ $\mathrm{cm}^{-1}$. In the $1 \times 1$ model, phonon hardening mainly occurred in the surface normal modes, and it is related to the $\mathrm{C} 2-\mathrm{C} 3$ bond strengthening in the $1 \times 1$ model. On the other hand, in the $2 \times 1$ model, by Ni adsorption, phonon softening occurred in the surface in-plane modes in 1300-1400 cm-1, which is related to the weakening of the $\mathrm{C} 1-\mathrm{C} 1^{\prime} \pi$-bond (Pandey chain). It is also found that the $\mathrm{Ni}-\mathrm{C}$ stretching mode frequencies are higher in the $1 \times 1$ model than $2 \times 1$ model, which is associated with the formation of a stronger $\mathrm{M}-\mathrm{C}$ bond in the $1 \times 1$ model rather than the $2 \times 1$ model.

Based on results of $\mathrm{Ni} / \mathrm{C}(111)$ in previous chapters, we investigated the other transition metals in the periodic table, hoping
that the new role of the Ni catalyst would also occur in other transition metals as well. As a result, we found that the metal elements in the center region of the periodic table (groups 4, 5, 6, 7, 8, 9, and 10) more favor the $1 \times 1$ model than the $2 \times 1$ model as an interfacial structure. It was found that this trend is related to the $\mathrm{C} 2-$ C3 bond length change of the $1 \times 1$ model and the $\mathrm{C} 1-\mathrm{C} 1^{\prime} \pi$-bond length change of the $2 \times 1$ model. It is noted that this catalytic trend is very related to the $M-C$ bond strength, and the $M-C$ became stronger as we go to the center region. By the electronic structure calculation, we can see that the reason why the $M-C$ bond is strong in the center. This is because the $d_{z^{2}}$ band of the metal element has the strongest interaction with the $p_{z}$ band of the diamond surface atom at the center region in the periodic table.

From the experimental results, it can be seen that the elements of group 8 such as Fe, Co, and Ni proposed by Generic Electric in the 1950 s enter the calculated boundary well. Mn (gropu 7) is the most stable $1 \times 1$ structure-forming element from the calculation results, but, practically, it needs higher temperature and pressure than Fe , Co, and Ni . It seems that Mn is advantageous in nucleation but disadvantageous in growth because a strong Mn-C bond in Mn/C (111) may be an obstacle for continuous surfactant-mediated growth.

Although early transition metals such as groups 3, 4, 5, and 6 seem likely to be good catalysts by having relatively moderate $\mathrm{M}-\mathrm{C}$ bonds, it is not doing so well because of stable carbide formation. In the calculation results, it is found that in the case of groups $3,4,5$, 6 , it is more stable to form MC carbide than $M / C$ (111) surface.

In the case of groups 11 and 12 , the catalyst effect is strongest in Cu and is shown in the order of Cu and Zn . This fits well with the experimental results provided by Kanda et al..

Lastly, we studied the catalytic role of excess charge on the diamond surface in the CVD system. To study the charged system within the PBC condition, the Plane-wave (PW) basis set and the atomic orbital (AO) basis set were compared. There is an inherent problem with the PW method when calculating the excess charged system under PBC conditions. As the vacuum size was increased, potential wells were created in the vacuum region due to electrostatic influences, and electrons escaped into this artificial potential well in the vacuum region. To solve this problem, the AO method was considered, and in the AO method, electrons did not escape into the vacuum due to the locality of atomic orbitals. Therefore, the behavior of charging in a large vacuum cell could be obtained using the AO method.

As the vacuum was increased, the electrostatic interaction between the adjacent cells became smaller, and as a result, the amount of charge inside the slab was reduced and most of the charges were concentrated on the surface-most site. As a result, in a large vacuum cell, it only affected the length of the $\mathrm{C} 1-\mathrm{C} 2$ bond on the surface, but not the C2-C3 bond. Accordingly, the energy change was very small. On the other hand, in the small vacuum cell, the charges were forcibly penetrated to the inside surface and affected the C2-C3 bond in the subsurface region. In other words, in an environment such as HWCVD, where many charges exist in the
vacuum unlike normal conditions, strong charging may be possible inside the surface, which will influence the C2-C3 bond in the subsurface region and stabilize the diamond $s p^{3}-$ like structure. In this perspective, the stability of the diamond seems to be related to the charge density in the vacuum. We need a more sophisticated method to interpret the charge effect on the diamond surface.

Through these studies, we know that it is important to understand the surface structure of diamonds and their reactive behaviors for both HPHT and CVD processes. We found that the transition metals form the $\mathrm{M}-\mathrm{C}$ bond on the diamond surface and change the interfacial structure. The stability of the diamond is directly associated with the charge redistribution caused by metal adsorption on the diamond surface. In addition, it was also found that the stability of the diamond surface may be influenced or changed by the excess charge supplied by the gas-activation system and it may depend on external charge density in the vacuum chamber. We expect these results will be useful to design an advanced diamond synthesis precess

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## Abstract in Korean

인공 다이아몬드 합성법은 1950년대 미국의 Generic Electric 사가 지구 내부의 환경을 모사한 고온고압법(High-Pressure and HighTemperature, HPHT)을 성공시킴으로써 시작되었다. 그 이후로 1970-80년대에 플라즈마나 고온-필라멘트를 이용한 화학적 기상 증착법 (Chemical Vapor Deposition, CVD)을 개발함으로써 진공 챔버에서 박막 형태의 다이아몬드를 형성하여 공업적으로 필요한 다양한 표면처리에 이용할 수 있었다. 고온고압법에는 반드시 $\mathrm{Fe}, \mathrm{Co}, \mathrm{Ni}$ 과 같은 촉매 금속이 필요한데, 현재까지 알려진 촉매금속의 주요한 역할은 흑연과 같은 탄소원을 용해하는 용매의 역할로써, 촉매금속의 탄소용해도와 녹는점을 촉매금속 선택의 주요 인자로 생각하였다. 하지만, 탄소용해도와 녹는점 만으로는 해결되지 않는 여러가지 실험결과들로 인해 새로운 추가적인 해석 인자를 필요로 하게 되었다. 또한, 화학적 기상 증착법에서 다이아몬드 형성을 촉진하는 과잉 전하의 역할에 대해 명확히 밝혀지지 않았다. 본 연구에서는 이러한 다양한 인공 다이아몬드 제조법에서 아직 밝혀지지 않은 촉매효과에 대해서, 제일원리 계산방법을 통해서 그 원리에 대해서 연구하였다.

첫번째로, Ni 의 다이아몬드 (111) 표면 위에서의 흡착 거동과 그에 따른 구조 변화에 대해서 알아보았다. 계산 결과에 따르면 다이아몬드 (111) 표면 위 Ni 이 흡착할 경우, 그 계면 안정 구조가 $1 \times 1$ 구조로 변하며, 이것은 Ni 이 흡착하지 않은 순수한 형태의 다이아몬드 (111) 표면구조가 $2 \times 1$ 구조인 것과 극명히 대비된다. 또한, Ni 이 흡착된 다이아몬드 (111) 표면의 성장 원리에 대하여 화학반응 경로를 계산하였다. 그 결과 Ni 원자는 항상 계면활성물질로써 탄소 원자와

교환작용을 통해 다이아몬드 (111) 표면이 지속적으로 성장이 가능함을 보였다.

두번째는, 앞서 연구한 Ni 이 흡착된 다이아몬드 (111) 표면의 포논 거동에 대해 이해하기 위해서, 범밀도함수 섭동 이론을 이용하여 각 구조에 대해서 포논상태밀도를 계산하였다. $1 \times 1$ 구조와 $2 \times 1$ 구조에 대해 Ni 의 흡착은 유의미한 포논상태밀도의 차이를 보였다. 포논모드 분석을 진행한 결과, 각 구조에서 Ni 의 흡착은 특정 포논모드들의 진동수를 변화시켰다. 이러한 특징들은 이전에 설명된 제일원리 계산을 통한 Ni 흡착에 따른 다이아몬드 (111)의 표면구조변화와 잘 일치하는 결과이다. 이러한 결과를 통해서 앞으로 광학적 측정을 통해서 다이아몬드에서의 촉매효과를 확인할 수 있을 것이다.

세번째는. 앞서 Ni 의 경우로 알아본 다이아몬드 (111) 표면에서의 촉매효과를 주기율표의 모든 전위금속들에 대해 확대하여 그 영향을 알아보고자 하는 것이다. 우리는 제일원리 전자구조 계산을 통해서 주기율표의 중앙에 위치하는 $(4,5,6,7,8,9,10$ 족) 원소들은 $1 \times 1$ 계면 구조를 형성하고, 반면에 주기율표의 가장자리에 위치하는 (3, 11, 12 족) 원소들은 $2 \times 1$ 계면 구조를 형성한다는 것을 알았다. 그 이유에 대해 알아보기 위해 전자구조 분석을 실행한 결과 전위금속의 d -밴드의 평균 위치, 전자 분포, 등이 금속마다 차이가 있기 때문에, 그로 인한 금속과 다이아몬드 표면의 상호작용이 차이가 생기기 때문이었다. 한편, 탄화물(carbide)과 표면 필름 생성 $[\mathrm{M} / \mathrm{C}(111)]$ 의 차이에 대해서 필름 생성 에너지를 계산한 결과 주기율표의 왼쪽에 있는 원소들 $(3,4,5,6$ 족) 은 표면 필름생성보다는 탄화물 생성이 더 쉽다는 것을 알았다. 이로 인해 3, 4, 5, 6족의 금속원자들은 표면에서 촉매효과를 일으키기가 어렵게 됨을 알았다. 이로써 촉매금속의 선정시에 지금까지 고려되었던 탄소용해도와 금속의 녹는점 뿐만 아니라 다이아몬드 표면에서의 금속의

표면작용이 촉매효과와 관련이 있는 새로운 인자 라는 것을 알았다.
마지막으로는, 화학적 기상 증착법에서 플라즈마나 고온필라멘트에서 주로 발생하는 과잉 전하들의 촉매작용에 대해서 알아보았다. 과잉전하가 다이아몬드 (111) 표면에 미치는 영향을 알아보기 위해 제일원리 계산을 이용하였다. 또한, 주기적 경계 조건 (Periodic Boundary Condition, PBC )에서 평면파 기저 (plane wave basis)를 사용할 경우 발생하는 인위적 오류에 대해서도 알아보았다. 계산 결과, 주기적 경계 조건을 사용시에는 평면파 기저 보다는 원자 오비탈 기저 (Atomic orbital basis)를 사용하는 것이 인위적으로 발생하는 진공으로 전하가 방출되는 현상을 억제할 수 있었다. 원자 오비탈 기저를 사용하여 계산을 진행한 결과, 진공의 크기에 따라 표면에 쌓이는 전하의 양이 달라졌는데, 매우 큰 진공 $(640 \AA$ ) 조건에서 수렴된 결과를 얻을 수 있었다. 하지만 진공이 클수록 내부의 전하량이 줄어들고 극 표면으로 전하가 모두 몰리게 되어, 전하에 의한 표면구조변화는 미미하였다. 반면에 매우 작은 진공 $(10 \AA)$ 조건에서는 주기적 경계 조건에 의한 옆 셀과의 정전기적 상호작용에 의해 다이아몬드 표면 내부로 과잉 전하가 스며들 수 있었고 그에 따라 유의미한 표면구조의 변화가 발생하였다. 음의 전하에 대해서는 $1 \times 1$ 구조의 $\mathrm{C} 2-\mathrm{C} 3$ 결합 길이가 짧아졌고, 양의 전하에 의해서는 $1 \times 1$ 구조의 $\mathrm{C} 2-\mathrm{C} 3$ 결합 길이가 길어졌다. 그러므로 음의 전하에 대해서 $s p^{3}$ 하이브리드 결합 구조를 갖는 것이 더 안정됨을 알 수 있었다. 매우 작은 진공조건 $(10 \AA)$ 에서만 이러한 표면구조변화가 생긴다는 것은 과잉전하효과가 일반적인 상황에서는 일어나기 힘들다는 것이며, 플라즈마나 고온-필라멘트와 같이 기상에 과잉전하가 매우 높은 밀도로 존재하는 조건들에서만 과잉전하에 의한 표면효과를 관찰할 수 있을 것으로 해석된다. 관련 해석에 관해서는 추가적인 연구가 더 필요하다.

