Effect of Nitrogen on the Growth of (100)-, (110)-, and (111)-Oriented Diamond Films

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Featured Application: This paper details the growth mechanism of (100)-, (110)-, and (111)-oriented nitrogen-doped diamond films.

Abstract: The aim of this research is the study of hydrogen abstraction reactions and methyl adsorption reactions on the surfaces of (100), (110), and (111) oriented nitrogen-doped diamond through first-principles density-functional calculations. The three steps of the growth mechanism for diamond thin films are hydrogen abstraction from the diamond surface, methyl adsorption on the diamond surface, and hydrogen abstraction from the methylated diamond surface. The activation energies for hydrogen abstraction from the surface of nitrogen-undoped and nitrogen-doped diamond (111) films were $-0.64$ and $-2.95$ eV, respectively. The results revealed that nitrogen substitution was beneficial for hydrogen abstraction and the subsequent adsorption of methyl molecules on the diamond (111) surface. The adsorption energy for methyl molecules on the diamond surface was generated during the growth of (100)-, (110)-, and (111)-oriented diamond films. Compared with nitrogen-doped diamond (100) films, adsorption energies for methyl molecule adsorption were by 0.14 and 0.69 eV higher for diamond (111) and (110) films, respectively. Moreover, compared with methylated diamond (100), the activation energies for hydrogen abstraction were by 0.36 and 1.25 eV higher from the surfaces of diamond (111) and (110), respectively. Growth mechanism simulations confirmed that nitrogen-doped diamond (100) films were preferred, which was in agreement with the experimental and theoretical observations of diamond film growth.

Keywords: diamond; nitrogen doping; hydrogen abstraction; adsorption energy; first-principles calculation

1. Introduction

Diamond consists of carbon atoms and has physical properties such as a low coefficient of friction [1], a high mechanical hardness of 100 GPa (75.5–111.5 GPa for diamond films), a high bulk modulus of $1.2 \times 10^{12}$ N/m$^2$, a high thermal conductivity of 20 W/cm-K (10 W/cm-K for diamond films), a thermal expansion coefficient of $0.8 \times 10^{-6}$/K, high electrical resistivity of $10^{16}$ Ω·cm, and a high energy bandgap of 5.47 eV [2]. Diamonds are employed in technical fields to accomplish tasks such as cutting, wear resistance coatings [3], and fabricating semiconductor components [4]. To prepare synthetic diamonds, Sussmann et al. used chemical vapor deposition (CVD) with methane, oxygen, and hydrogen [5] mixed in a specified ratio. Hot filament (HF) CVD, microwave plasma (MP) CVD, and MP-enhanced CVD have since been used for the growth of diamond films [6–8].

In 1993, Singh and Vellaikal proposed the following process for the nucleation of diamonds: carbon atoms first aggregate into carbon clusters, and the $sp^2$ bonds between carbon atoms are then transformed into $sp^3$ bonds at high pressure, which results in the carbon clusters forming a diamond structure [9]. The diffusion of carbon atoms on the
diamond surface is the key factor influencing the growth rate of diamonds. In 2005, Tamura et al. studied nucleation on the diamond (100) surfaces with methyl molecules (CH$_3$) and hydrogen ions fabricated through CVD [10]. Their results revealed the three steps through which diamond nucleation occurs. The hydrogen abstraction from the diamond (100) surface is assumed to take place by using a hydrogen radical, resulting in a gaseous H$_2$ molecule. A schematic of this mechanism of nucleation is shown in Figure 1a–c. Second, a methyl molecule is adsorbed by the dangling surface bond, and a hydrogen atom of the methyl molecule is freed by atomic hydrogen in the chamber. Figure 1d–f show the schematic for hydrogen abstraction from a methyl molecule on the diamond surface. Finally, the C–C dimer breaks and forms a new ring with the methylene molecule on the diamond surface. A schematic of the breaking dimer and ring formation is shown in Figure 1g–i. According to these findings, the hydrogen extraction from methyl molecules on the diamond surface is crucial for the diamond growth rate. In 2011, Ali et al. used the HFCVD technique to deposit diamond films with various methane concentrations [11]. Their experimental results suggested that methyl molecules are the main source of diamond growth.

![Figure 1](image_url)

**Figure 1.** (Color online) (a) A hydrogen atom approaches the hydrogen-terminated C–C dimer of the diamond surface; (b) The terminated hydrogen atom is extracted from the transition state; (c) This forms a hydrogen molecule away from the diamond surface. (d) A methyl molecule is bonded to the diamond surface; (e) The hydrogen atom of this methyl molecule is extracted from the transition state; (f) This forms a methylene molecule on the diamond surface and a hydrogen molecule away from the diamond surface. (g) Finally, a methylene molecule approaches; (h) This methylene molecule causes the C–C dimer in the pentagon carbon ring to break; (i) This pentagon carbon ring becomes a hexagon carbon ring. White and gray spheres represent H and C atoms, respectively.

The primary impurity in diamonds is nitrogen [12]. In 2004, Chayahara et al. first used 2.45-GHz MPCVD with methane at 60 standard cubic centimeters per minute (sccm) and hydrogen at 500 sccm. They observed that the diamond growth rate ranged from 30 to 120 µm/h. Furthermore, to understand the effect of nitrogen on the growth of diamond
films, nitrogen gas was added at 1.8 sccm, which doubled the diamond growth rate. Therefore, nitrogen doping increases the growth rate of diamonds [13]. In 2008, Regemorter et al. studied the effect of nitrogen on the initial stages of diamond growth using CVD and determined the reaction energies of nitrogen-doped diamond (100) and (111) surfaces [14]. Their results indicated that the hydrogen abstraction energy can be reduced when nitrogen is added to the system. Numerous experiments have been conducted on nitrogen-doped diamonds, but the influence of nitrogen doping on diamond growth is not yet fully understood. Therefore, on the basis of density-functional theory, we systematically studied the reaction energies of nitrogen-doped (100)-, (110)-, and (111)-oriented diamond films.

2. Structure and Computational Methods

To study the reaction energy of a nitrogen-doped diamond surface, we used the implementation of density-functional theory in the Vienna ab initio simulation package (VASP) [15,16] with the generalized gradient approximation (GGA) [17,18] for the exchange correlation functional. We prepared supercell (VASP) [15,16] with the generalized gradient approximation (GGA) [17,18] for the exchange correlation functional. We prepared supercell $C_{72}H_{24}$ containing 72 carbon atoms and terminated with 24 hydrogen atoms on both sides, as depicted in Figure 2, for the (100)-, (110)-, and (111)-oriented surfaces. The Monkhorst–Pack scheme included $k$-meshes of $4 \times 3 \times 1$, $3 \times 3 \times 1$, and $3 \times 2 \times 1$ for the (100), (110), and (111) surfaces, respectively. The cut-off energy was set to 400 eV, and the self-consistent total energy criterion was $10^{-5}$ eV.

![Figure 2](image-url) (Color online) Supercell structures used for diamond (100) surface, diamond (110) surface, and diamond (111) surfaces. Each surface contains 24 hydrogen atoms and 72 carbon atoms. The letters A, B, C, and D denote positions of nitrogen atoms. White and gray spheres represent H and C atoms, respectively.

To calculate the hydrogen extraction energy $E_{ex}^H$ (eV), we used the following formula:

$$E_{ex}^H = (E_{product} + E_{iso}^{H_2}) - (E_{reactant} + E_{iso}^H),$$  \hspace{1cm} (1)

where $E_{product}$ is the total energy produced by extracting a hydrogen atom from the surface of a H-terminated diamond slab $C_{72-x}H_{23}N_x$ ($x = 0, 1$), $E_{iso}^{H_2}$ is the total energy of an isolated H$_2$ molecule, $E_{reactant}$ is the total energy of a H-terminated diamond slab $C_{72-x}H_{24}N_x$ ($x = 0, 1$), and $E_{iso}^H$ is the total energy of an isolated hydrogen atom. We calculated $E_{ex}^H$ for the substitution of a nitrogen atom in positions A, B, C, or D for the diamond (100), (110), and (111) surfaces shown in Figure 2. After the hydrogen atom escaped from the diamond surface, we calculated $E_{ad}^{CH_3}$, the molecule adsorption energy of CH$_3$ as follows:

$$E_{ad}^{CH_3} = E_{surface-CH_3} - (E_{product} + E_{iso}^{CH_3}),$$  \hspace{1cm} (2)

where $E_{surface-CH_3}$ is the total energy of a diamond slab after reacting with a methyl radical $C_{73-x}H_{26}N_x$ ($x = 0, 1$), and $E_{iso}^{CH_3}$ is the total energy of an isolated CH$_3$ molecule.
We also calculated $E_{CH_3}^{ad}$ for situations in which a nitrogen atom is absorbed into the inner layer of the diamond slab. Furthermore, we calculated $E_{H_{abstr}}^H$, the energy required for hydrogen abstraction from the methylated diamond surface, as follows:

$$E_{H_{abstr}}^H = (E_{surface}^{CH_2} + E_{H_2}^{iso}) - (E_{surface}^{CH_3} + E_{H_2}^{iso}), \quad (3)$$

where $E_{surface}^{CH_2}$ is the total energy of a diamond slab after reacting with a methyl radical $(CH_2)$, $C_{73-x}H_{25}N_x \ (x = 0, 1)$. Finally, we also calculated the hydrogen extraction energy for a $CH_3$ molecule for various nitrogen–substitution positions.

3. Results and Discussion

The hydrogen extraction energies from diamond (100), (110), and (111) surfaces with and without nitrogen doping are listed in Table 1. The calculated hydrogen extraction energies for diamond (100), (110), and (111) surfaces were $-0.53$, $-0.84$, and $-0.64$ eV, respectively. The (110) diamond surface had the lowest hydrogen extraction energy of $-0.84$ eV. When the inner layer is nitrogen doped, the hydrogen extraction energy decreased. For example, if the second layer is nitrogen doped, then the hydrogen extraction energies from diamond (100), (110), and (111) surfaces were $-2.35$, $-2.03$, and $-2.45$ eV, respectively. $E_{H_{ex}}^H$ was one order of magnitude smaller than the corresponding value on the diamond surface. The lowest hydrogen extraction energy of $-2.95$ eV was obtained when the third layer is nitrogen doped, which indicated that nitrogen-doped diamond (111) is favorable for hydrogen surface extraction. In general, hydrogen extraction energy considerably decreased after nitrogen doping.

| Hydrogen Extraction Energy (eV) | (100) | (110) | (111) |
|-------------------------------|-------|-------|-------|
| No doped                      | $-0.53$ | $-0.84$ | $-0.64$ |
| N in position A               | $-2.35$ | $-2.03$ | $-2.45$ |
| N in position B               | $-1.52$ | $-1.65$ | $-2.95$ |
| N in position C               | $-2.43$ | $-2.01$ |       |
| N in position D               |       |       | $-1.67$ |

Table 2 lists the methyl molecule adsorption energies $E_{CH_3}^{ad}$ for the diamond (100), (110), and (111) surfaces. The $E_{CH_3}^{ad}$ values were $-4.66$, $-3.39$, and $-4.18$ eV for the diamond (100), (110), and (111) surfaces, respectively. The lowest $E_{CH_3}^{ad}$ value was obtained for the diamond (100) surface, indicating that attachment of $CH_3$ to the diamond (100) surface was favorable. A previous study reported a lower result of $E_{CH_3}^{ad}$ for the diamond (100) surface, with $E_{CH_3}^{ad} = -3.72$ eV [14]. When the diamond layer was nitrogen doped, $E_{CH_3}^{ad}$ substantially increased. This suggested that nitrogen doping does not favor the methyl molecule adsorption. Nevertheless, methyl group adsorption is crucial for the growth of artificial diamonds. On the basis of the hydrogen extraction energy and methyl group adsorption energy, we determined the total energy required for hydrogen abstraction and methyl molecule adsorption. The lowest sum of $-5.19$ eV was obtained for the diamond (100) surface. However, nitrogen is the most common impurity in diamonds. In this situation, when nitrogen was doped to position C of the diamond (100) surface, this energy was $-4.18$ eV (Figure 2; Tables 1 and 2).
Table 2. Methyl molecule adsorption energy $E_{\text{ad}}^{\text{CH}_3}$ for the diamond (100), (110), and (111) surfaces with or without nitrogen doping at positions $A$, $B$, $C$, and $D$.

| Adsorption Energy (eV) | (100) | (110) | (111) |
|------------------------|-------|-------|-------|
| No doped              | −4.66 | −3.72 * | −3.39 | −4.18 | −3.29 * |
| N in position $A$     | −1.84 | −1.78 * | −1.26 | −1.54 | −1.30 * |
| N in position $B$     | −2.46 | −2.46 * | −1.77 | −1.01 |        |
| N in position $C$     | −1.75 | −1.38 |       |       |        |
| N in position $D$     | −2.32 |       | −2.32 |       |        |

* Ref. [14].

After $\text{CH}_3$ is adsorbed into the diamond surface, the next step for diamond growth is hydrogen extraction from the methyl group. Table 3 lists the hydrogen extraction energy from $\text{CH}_3$ for the diamond (100), (110), and (111) surfaces. First, for diamond (100), (110), and (111) surfaces, $E_{\text{abstr}}^{\text{H}}$ was calculated as $−0.72$, $−0.81$, and $−0.54$ eV, respectively. $E_{\text{abstr}}^{\text{H}}$ decreased after nitrogen doping, signifying that nitrogen doping is facilitated hydrogen extraction from the methyl molecule.

Table 3. Methyl group hydrogen extraction energy $E_{\text{abstr}}^{\text{H}}$ for the diamond (100), (110), and (111) surfaces with or without nitrogen doping at positions $A$, $B$, $C$, and $D$.

| Hydrogen Extraction Energy $E_{\text{abstr}}^{\text{H}}$ (eV) | (100) | (110) | (111) |
|---------------------------------------------------------------|-------|-------|-------|
| No doped                                                      | −0.72 | −0.27 * | −0.81 | −0.54 | −0.22 * |
| N in position $A$                                             | −3.05 | −1.87 * | −1.77 | −2.69 | −2.72 * |
| N in position $B$                                             | −1.78 | −1.43 * | −1.80 | −1.52 |        |
| N in position $C$                                             | −1.62 |       | −1.53 | −1.37 |        |
| N in position $D$                                             |       |       |       |       |        |

* Ref. [14].

The lowest $E_{\text{abstr}}^{\text{H}}$ value of $−3.05$ eV was recorded with nitrogen doping in position $A$ on the diamond (100) surface. $E_{\text{abstr}}^{\text{H}}$ was calculated as $−0.72$ and $−0.54$ eV for the diamond (100) and (111) surfaces, respectively, which were in close agreement with previous theoretical results of $−0.27$ and $−0.22$ eV [14], respectively.

Table 4 lists the total energies of hydrogen abstraction from the diamond surface $E_{\text{ex}}^{\text{H}}$, methyl molecule adsorption on the diamond surface $E_{\text{ad}}^{\text{CH}_3}$, and hydrogen abstraction from the methylated diamond surface $E_{\text{abstr}}^{\text{H}}$ (i.e., $E_{\text{ex}}^{\text{H}} + E_{\text{ad}}^{\text{CH}_3} + E_{\text{abstr}}^{\text{H}}$). The diamond (100) surface yielded the lowest total energy of $−5.91$ eV. After nitrogen doping at position $A$, the total energies of the diamond (100) or (111) surfaces decreased, indicating that nitrogen impurities are beneficial for diamond growth. The lowest total energy of $−7.24$ eV was obtained for nitrogen doping at position $A$ on the diamond (100) surface. The hydrogen extraction energy from the methyl molecule yielded the greatest contribution to this total. Furthermore, for the diamond (111) surface, the total energy was $−6.68$ eV after nitrogen doping in position $A$.

To further clarify the impact of near-to-surface nitrogen doping on the hydrogen extraction energy, we plotted four models of the nitrogen doping through substitutional nitrogen exchange with a neighboring vacancy in Figure 3. In Figure 3a, the reference energy is set for a free nitrogen atom and the diamond (100) surface with a single vacancy. In Figure 3b, the chemisorption of the nitrogen atom on the diamond (100) surface yields an energy gain of $−0.56$ eV. Then, the adsorbed nitrogen atom diffuses into the inner layer of the diamond (100) surface at position $A$ or $B$ (Figure 2), which requires a low energy addition of $0.07$ eV, as illustrated in Figure 3c. Position $A$ or $B$ is a transition state with a low barrier height for the nitrogen migration towards the inside of the diamond layers for a
favorable driving force of $-1.11$ eV as shown in Figure 3d, showing that the nitrogen atom moves from position A or B to position C (Figure 2), with an energy gain of $-1.11$ eV. This demonstrated that the energy of $-1.11$ eV can promote the diffusion of doped nitrogen.

Through the vacancy diffusion mechanism, this result is in full agreement with the previous experiments on nitrogen-doped diamond surfaces [12–14].

Figure 3. (Color online) (a) Nitrogen exposure and (b) chemisorption of a nitrogen atom on the diamond surface; nitrogen substitution on the (c) second and (d) third layers of the diamond surface. The stoichiometry of all super cells was fixed at $C_{71}H_{23}N_1$. Blue, white, and gray spheres represent N, H, and C atoms, respectively. Dashed circles indicate vacancies.
Table 4. Total energy for the three main steps of diamond growth. Hydrogen abstraction from the diamond surface $E_{Hex}^H$, methyl molecule adsorption on the diamond surface $E_{CH3}^{ad}$, and hydrogen abstraction from the methylated diamond surface $E_{abstr}^H$.

|                  | (100)  | (110)  | (111)  |
|------------------|--------|--------|--------|
| No doped         | −5.91  | −5.04  | −5.36  |
| N in position A  | −7.24  | −5.06  | −6.68  |
| N in position B  | −5.76  | −5.22  | −5.48  |
| N in position C  | −5.80  | −4.92  | −5.36  |
| N in position D  | −5.36  | −      | −      |

4. Conclusions

Based on the framework of density-functional theory, we investigated hydrogen extraction and methyl adsorption for (100)-, (110)-, and (111)-oriented diamond films with and without nitrogen doping.

The activation energies of hydrogen abstraction for nitrogen-undoped and nitrogen-doped diamond (111) surfaces were −0.64 and −2.95 eV, respectively. The results indicated that nitrogen substitution in the diamond (111) film are beneficial for hydrogen abstraction and for the subsequent adsorption of methyl molecules. Compared with nitrogen-doped diamond (100) films, adsorption energies for methyl molecule adsorption were by 0.14 and 0.69 eV higher for diamond (111) and (110) films, respectively. Furthermore, compared with methylated diamond (100) films, activation energies for hydrogen abstraction were by 0.36 and 1.25 eV higher for diamond (111) and (110) films, respectively. The simulations confirmed that nitrogen-doped diamond (100) films are preferred, which was in agreement with experimental and theoretical observations of diamond film growth.

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