The Surface Effect on the Growth of Related Color Centers in Diamond

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Abstract. In this paper, the growth of SiV and NV centers in the different atomic layers of different surface in diamond is studied through first-principles calculations. It is revealed that, the formation energy of SiV and NV centers at the surface is lower than in the bulk. That is to say, SiV and NV centers are formed more easily at the surface, SiV and NV centers in the surface region is more stable than in the bulk. All these results strongly indicate that the interaction between diamond surfaces and the SiV and NV centers play a critical role during the incorporation of SiV and NV centers in the CVD process. It is the significant foundation for improving the growth of related color centers and it is very important for the formation and control of related defects in the epitaxial growth of diamond. Due to the different surface energy and property, the growth of SiV and NV centers is different on different surfaces.

1. Introduction
Quantum information is becoming more and more important to us, which has inspired more and more scientists are devoted to the research of quantum information. In recent years, due to its stable fluorescence, unique physical and chemical properties, diamond crystals have become an excellent platform for solid quantum information processing (QIP) and quantum information science, especially color centers in diamond, which are light stable solid single photon sources at room temperature. Diamond plays an important role in quantum information applications, it mainly because that it can host many color centers. In recent years, owing to its unique property, colour centres in diamond have been proven to have the potential to fulfil the requirements for the practical application [1].

It has been documented more than 500 color centers in diamond so far [2, 3, 4]. The majority of the well-known color centers are silicon vacancy (SiV) center and nitrogen vacancy (NV) center, the performance of which, deliver superior fluorescence properties [5, 6, 7, 8, 9].

In this paper, based on first-principles calculations, we studied the growth of SiV and NV centers in the different atomic layers of different surface in diamond. It is revealed that the surfaces are important platforms for the growth of Si/N related defects in diamond. SiV and NV centers are formed more easily at the surface, SiV and NV centers in the surface region is more stable than in the bulk. Besides, the growth of SiV and NV centers in diamond depends on the orientation of the surface. Both the SiV centers and NV centers have different preferential orientations grown on different surfaces in diamond. All these results are indispensable to the researchers in and beyond the field of practical application of related color centers.
2. Computational method and computational model

2.1. Computational method
We use the spin-polarized calculations based on density-functional theory, which is implemented by the Vienna Ab initio Simulation Package (VASP) [10] software package, that is to say, we consider the effect of spin polarization (ISPIN=2) when calculating the formation energy of all related color centers. During this work, the pseudopotential is realized by applying the method of projector-augmented-wave (PAW) method and the exchange-correlation functional is realized by PBE [11]. The cut-off energy is set to 400 eV, and the k-point grid is 2 x 2 x 1 [12, 13].

2.2. Computational model
During calculation, all different diamond surfaces is modeled by slab. The (110) diamond surface, of which the structure is shown in Fig. 1 (a), is modeled by a slab with 3x4 surface cell (parallel to the surface) and 9 layers of C atoms (perpendicular to the surface). Similarly, the (100) diamond surface (as shown in Fig. 1 (b)) is modeled by a slab with 4x4 surface cell and 14 layers of C atoms; the (111) diamond surface (as shown in Fig. 1 (c)) is modeled by a slab with 4x4 surface cell and 12 layers of C atoms [14].

![Figure 1. The atomic structures of different surfaces in the diamond. (a) (110) surface, (b) (100) surface, (c) (111) surface. The brown and pink balls are C and H atoms, respectively. The numbers in the surface represent different atomic layers of different surface in diamond.](image)

The top and bottom of the Slab are made of the same atoms (carbon), and one of the surfaces (top) is used to simulate the actual computing system. At the same time, in order to avoid the interaction between the unsaturated bonds of carbon atoms at the bottom of the slab and the surface electron states at the top of the slab under the condition of periodic boundary, we passivated all of them with hydrogen atoms, which met the 8-N principle. In addition, we add vacuum layer in the vertical direction on the surface of the slab model with the thickness of 12 Å. In the process of surface structure optimization, carbon atoms at the 4 bottom atomic layers of the slab are fixed to simulate the bulk, and all the other carbon atoms are allowed to relax until the forces are smaller than 0.01 eV/Å.

3. Results and discussion

3.1. The stability of SiV and NV centers on the (110) surface in diamond
First, we calculate the formation energy of SiV and NV center in different areas of diamond (110) surface. During the calculation, the formation of related color centers can be expressed by the following expression:

$$E_f = E_{tot} - E_s + n \cdot \mu_C - m \cdot \mu_{Si} \left( \mu_N \right) + l \cdot \mu_H$$

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where $E_{\text{tot}}$ is the total energy of the surface supercell with the related color centers; $E_s$ is the total energy of the corresponding supercell diamond surface which is fully hydrogenated and acts as a reference; $\mu_C (\mu_{Si}, \mu_{N}, \mu_{H})$ is the chemical potential of C (Si, N, H); $\mu_C$ is the chemical potential of carbon, which is calculated as in bulk diamond; $\mu_{Si}$ as in gas SiH$_4$, i.e., $\mu_{Si} + 4\mu_{H}$ equals to the total energy of an isolated SiH$_4$; $\mu_{N}$ as in gas N$_2$. During calculation, the value of $\mu_H$ can be taken with different values depending on the growth environment. The $\mu_H$ value of 0 in this paper represents H$_2$ gas state and -0.36 eV the CH$_4$ gas state with $\mu_C$ as of bulk diamond [12]. In order to form the related color centers, we removed n (l) C (H) atoms from the reference surface, and m is the number of Si/N atoms at the surface.

Table 1. The formation energy of SiV and NV centers at different atomic layers on (110) surface in diamond. The bulk values are also listed at the bottom for comparison. The 1–2, 2–3, 3–4 substitutional sites for SiV and NV centers at the surface are indicated in figure 1 (a)–(c).

| Diamond (110) surface | SiV location | NV location |
|----------------------|--------------|-------------|
|                      | Formation energy (0 eV) | Formation energy (0.37 eV) |
| 1-2                  | 4.49         | 2.64        | 1-2                  | 2.04         | 2.41 |
| 2-3                  | 5.23         | 4.12        | 2-3                  | 2.73         | 3.84 |
| 3-4                  | 5.84         | 4.36        | 3-4                  | 3.78         | 4.89 |
| bulk                 | 5.58         | bulk        |                       | 5.42         |      |

On the (110) surface in diamond, of which the structure is shown in Fig. 1(a), carbon atoms in the same atomic layer are equivalent. We propose a single Si or N atoms replace C atoms in different atomic layer, but the position of the vacancies can be either in the same carbon atomic layer with Si or N atoms, or in the adjacent two different carbon atomic layers. The symbol 1 represents both the Si/N atom and the vacancies are located in the same 1st carbon atomic layer; 1-2 represents the vacancies are located in the 1st carbon atomic layer and the Si or N atom located in the 2nd carbon atomic layer. Similarly, 2-3 represents the vacancies are located in the 2nd carbon atomic layer and the Si or N atom located in the 3rd carbon atomic layer; 3-4 represents the vacancies are located in the 3rd carbon atomic layer and the Si or N atom located in the 4th carbon atomic layer.

The formation energy of SiV and NV centers in different atomic layers on the hydrogenated (110) diamond surface is listed in Table 1. It can be found in the table that as the position of SiV and NV center gradually transitions from the surface atomic layer of diamond to the middle-layer (5 layers) of slab, its formation energy gradually increases, and when it reaches the middle-layer, its formation energy tends to be similar to that in bulk. This also indicates that, on the diamond (110) surface, SiV and NV center is easily to form at the surface. Such a trend of the formation energy changes with the surface atomic layer strongly indicates that SiV and NV centers are not easy to form in the middle atomic layer area, but rather tends to form in the surface area.

Our calculations also show that the favored SiV and NV centers should lie along one of the C-H bonds of the (110) surface, it is mainly because of the surface effect.

3.2. The stability of SiV and NV centers on the (100) surface in diamond

For diamond (100) surfaces, the most stable surface reconstruction is characterized by dimer rows, which means that each surface C atom is connected to an H atom, and the four axes of diamond can appear alternately on the surface [15,16,17]. Due to such a surface effect, the orientation of the formed
SiV and NV centers SiV also follows the C-H bond axes of the surface, which among the four sp3 bond axes of diamond.

Table 2. The formation energy of SiV and NV centers at different atomic layers on (100) surface in diamond. The bulk values are also listed at the bottom for comparison. The 1–2, 2–3, 3–4 substitutional sites for SiV and NV centers at the surface are indicated in figure 1(a)–(c).

| Diamond (100) surface | Formation energy (E$_f$=0 eV) | Formation energy (E$_f$=-0.37 eV) | NV location | Formation energy (E$_f$=0 eV) | Formation energy (E$_f$=-0.37 eV) |
|----------------------|-----------------------------|---------------------------------|------------|-----------------------------|---------------------------------|
| SiV location         |                            |                                 |            |                            |                                 |
| 1-2                  | 2.45                       | 0.97                            | 1-2        | 0.7                        | 1.07                            |
| 2-3                  | 5.73                       | 4.62                            | 2-3        | 3.59                       | 4.33                            |
| 3-4                  | 6.05                       | 4.57                            | 3-4        | 3.94                       | 4.68                            |
| bulk                 | 5.58                       | bulk                            |            |                            |                                 |

Table 2 lists the formation energy of SiV and NV centers in different atomic layers on the hydrogenated (100) diamond surface. It can be seen from the table that SiV and NV centers are most stable at the first atomic layer. With the gradual growth to the deeper atomic layer, their corresponding formation energy increases gradually and converges to the value of bulk structure.

3.3. The stability of SiV and NV centers on the (111) surface in diamond

In addition to (110) surface and (100) surface, (111) surface are also often used for the growth of diamond by CVD method. The atomic structure of the (111) surface is quite different from (110) and (100) surface, and the surface is also hydrogenated under H enriched environment. For the diamond (111) surface, the most stable surface is non-reconstruction, which is also a surface carbon atom connected to a hydrogen atom, and only one bond along the surface normal line can appear on the surface [12,17]. The formation energy of SiV and NV centers in different atomic layers on the hydrogenated (111) diamond surface is listed in Table 3. The changing trend of the formation energy of SiV and NV centers on (111) surface is similar to the (110) and (100) surface.

Table 3. The formation energy of SiV and NV centers at different atomic layers on (111) surface in diamond. The bulk values are also listed at the bottom for comparison. The 1–2, 2–3, 3–4 substitutional sites for SiV and NV centers at the surface are indicated in figure 1(a)–(c).

| Diamond (111) surface | Formation energy (E$_f$=0 eV) | Formation energy (E$_f$=-0.37 eV) | NV location | Formation energy (E$_f$=0 eV) | Formation energy (E$_f$=-0.37 eV) |
|----------------------|-------------------------------|---------------------------------|------------|-----------------------------|---------------------------------|
| SiV location         |                              |                                 |            |                            |                                 |
| 1-2                  | 4.55                         | 2.7                             | 1-2        | 2.46                        | 2.83                            |
| 2-3                  | 5.9                          | 4.42                            | 2-3        | 3.17                        | 4.28                            |
| 3-4                  | 5.74                         | 4.25                            | 3-4        | 3.51                        | 4.62                            |
| bulk                 | 5.58                         | bulk                            |            |                            |                                 |
As shown in the table 3, surprisingly, the formation energy of SiV centers in 3-4 atomic layers are lower than that in 2-3 atomic layers, this indicates that on the (111) surface, SiV centers may prefer to form within one double-layer. Because there are three equivalent bond axes in diamond (111) surface for the growth of a one-step SiV centers, the SiV centers grown on (111) surface may have three possible orientations. Contrasting to that of SiV center, the formation energy of NV center in 3-4 atomic layers are higher than that in 2-3 atomic layers, which indicates that on the (111) surface, NV centers have only one preference orientation on the (111) surface.

4. Conclusion
Because of the surface effect, SiV and NV centers are easily to form on any surface in diamond, and are hardly to form in the bulk structure. The direction and number of unsaturated carbon atom bonds axes on different surfaces in diamond are various, which leads to different preference orientations and different amounts of preference orientations of SiV and NV centers in different surfaces in diamond. Researchers and experimenters in related fields can choose the suited diamond surface, which is more easily to grow SiV and NV centers, according to different experimental needs or production and living needs. Different SiV and NV centers in different preference orientations have quite different properties, that is, SiV and NV centers grown on the different surface in diamond have various advantages. The diamond surface used for SiV and NV centers can be selected according to the practical application in the future.

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