First-principles Studies of The Effect of H and F Decoration on The Growth of Silicon Vacancy on (100) Surface in Diamond

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Abstract. In this paper, the effect of H and F decoration on the growth of silicon vacancy on (100) surface in diamond has been studied. It is revealed that, the formation energy of SiV centers on (100) surface in diamond under different H/F coverages (1/4, 1/2, 3/4, and 1 ML) depending on the growth environment are various. SiV centers are more easily formed decorated with F in F–rich growth environment. Due to the different electronegativity of H and F, the growth of SiV centers is different. It plays a critical role for improving the growth of related color centers in and beyond the field of growth and application of color centers to the experimentalists.

1. Introduction

With the development of quantum physics and quantum information, single-photon sources play an important role and attract researchers’ interest. From quantum information processing to highly sensitive magnetometry [1, 2, 3] and cellular imaging [4] single-photon sources are critical. In recent years, studies show that silicon is a frequent accidental contaminant in CVD diamond. Owing to its unique properties of perfect photoluminescence stability and optically detectable electronic spin resonance, the silicon vacancy (SiV) color center in diamond has been inspired more and more scientists’ studies over the past few years[5, 6].

Diamond (100) surface grows the slowest in the process of chemical vapor deposition (CVD), and the surface is also the most controllable one [7]. The (100) surface has two suspension bonds, while the (111) and (110) surfaces have only one [8]. That is to say, of all the surfaces in diamond, the diamond (100) surface is the most chemically active and the most important one [9]. It also has been reported that the surface decoration of diamond has a great impact on the physical and chemical properties of nanodiamond. Therefore, the research on surface decoration is of great significance to the regulation of the optical properties of single-photon source devices of diamond.

In this paper, we studied the effect of H and F decoration on the growth of silicon vacancy on (100) surface in diamond through the first-principles calculations. Various types of chemical decoration have been applied to the surface of diamond (100), together with pure diamond. The geometrical configurations of (100) surface were compared and the influence of H and F on diamond growth was studied. It is revealed that decorated with different H or F coverages, the formation energy was different. All these results are indispensable to the researchers who devoted to the practical application of related color centers.
2. Computational method and computational model

2.1. Computational method
During this work, based on density-functional theory, the spin-polarized calculations (ISP(N=2)) which is implemented by the Vienna Ab initio Simulation Package (VASP) [10] software package was used when calculating the formation energy of all related defects. The pseudopotential in this work we use is 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
In this work, the (100) diamond surface, of which the structure is shown in Fig. 1, is modelled by a slab with 4 x 4 surface cell and 14 layers of C atoms.

![Diagram of (100) surfaces with a SiV center at the first layer in the diamond. The brown, blue and pink balls are C, Si and H atoms, respectively.](image)

Figure 1. The atomic structures of (100) surfaces with a SiV center at the first layer in the diamond. The brown, blue and pink balls are C, Si and H atoms, respectively.

During this slab, one of the surfaces (top) is used to simulate the actual computing system. The carbon atoms at the bottom surface are all passivated with hydrogen atoms and added with a vacuum layer with the thickness of 12 Å. During calculation, 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
In this paper, the formation of related defects can be expressed by the following expression:

\[ E_f = E_{tot} - E_s - \mu_H(m_H) \]

where \( E_{tot} \) is the total energy of the surface supercell with the related defects decorated with H or F; \( E_s \) is the total energy of the corresponding supercell diamond surface which acts as a reference; \( \mu_H (m_H) \) is the chemical potential of H (F); \( \mu_{Si} \) as in gas SiH4, i.e., \( \mu_{N} \) as in gas N2. During calculation, the value of \( \mu_H \) and \( \mu_F \) can be taken with different values depending on the growth environment. The H rich in this paper represents \( H_2 \) gas state and H poor is in the C \( H_4 \) gas state with \( \mu_C \) as of bulk diamond. That is to say, \( \mu_C + 4\mu_H \) equals to the total energy of an isolated CH4; \( \mu_C + 4\mu_F \) equals to the total energy of an isolated CF4.
Figure 2. The atomic structures of SiV centers on (100) surface in diamond under four hydrogen coverages (1/4, 1/2, 3/4, and 1 ML). Fig 2. (a) And (b) represent the top view and side view of SiV center under hydrogen coverage with 1/4 ML, respectively. Similarly, Fig 2. (C) and (d) represent SiV center under hydrogen coverage with 2/4 ML. Fig 2. (E) and (f) represent SiV center under hydrogen coverage with 3/4 ML. Fig 2. (g) And (h) represent SiV center under hydrogen coverage with 4/4 ML.

As shown in Fig 2 and Fig 3, the atomic structures of SiV centers on (100) surface in diamond under four hydrogen and F coverages (1/4, 1/2, 3/4, and 1 ML) are various.

Figure 3. The atomic structures of SiV centers on (100) surface in diamond under four F coverages (1/4, 1/2, 3/4, and 1 ML). Fig 3. (a) And (b) represent the top view and side view of SiV center under F coverage with 1/4 ML, respectively. Similarly, Fig 3. (C) and (d) represent SiV center under F coverage with 2/4 ML. Fig 3. (E) and (f) represent SiV center under F coverage with 3/4 ML. Fig 3. (g) And (h) represent SiV center under F coverage with 4/4 ML. The gray balls are F atoms.

The formation energy of SiV centers on (100) surface in diamond under four H/F coverages (1/4, 1/2, 3/4, and 1 ML) depending on the growth environment is listed in Table 1. It can be seen in the table that SiV centers are more easily formed in H-rich or F-rich compared with H-poor or F-poor. For H coverage, 1 ML was the most favored. While for F coverage, 2/4 ML was the most favored. It mainly because that the electronegativity of H and F are different.
Table 1. The formation energies of SiV centers on (100) surface in diamond under four H/F coverages (1/4, 1/2, 3/4, and 1 ML) depending on the growth environment.

| H Coverage (ML) | Formation energy (H-rich) | Formation energy (H-poor) | F Coverage (ML) | Formation energy (F - rich) | Formation energy (F - poor) |
|---------------|---------------------------|---------------------------|----------------|-----------------------------|-----------------------------|
| 1/4           | -1.62                     | -1.25                     | 1/4            | -3.28                       | -2.95                       |
| 2/4           | -1.56                     | -1.19                     | 2/4            | -3.43                       | -3.1                        |
| 3/4           | -1.69                     | -1.32                     | 3/4            | -3.25                       | -2.92                       |
| 4/4           | -1.82                     | -1.45                     | 4/4            | -3.37                       | -3.04                       |

4. Conclusion
SiV centers are more easily formed in F–rich growth environment. For the different electronegativity of H and F, the growth of SiV centers decorated with H and F is different. We proposed that SiV centers decorated with different chemical group may have various properties and formation energy. The chemical group used for decorating SiV centers can be selected according to the practical application in the future.

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