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Full Length Article

Adsorption and migration behavior of Si atoms on the hydrogen-terminated diamond (001) surface: A first principles study

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ABSTRACT

The adsorption and migration activation energies of a silicon (Si) atom on a hydrogen-terminated diamond (001) surface were calculated using first principles methods based on density functional theory. On the fully hydrogen-terminated surface, the surface carbon atoms possess saturated bonds. The Si atom cannot bond with the surface carbon atoms; thus, the adsorption energy of the Si atom is low. However, on the hydrogen-terminated surface with one or two open radical sites (ORS), the adsorption energy of a Si atom increases to 3.1 eV and even up to 4.7 eV, thereby forming a stable configuration. Along the three ORS in the direction of dimer row or chain, a Si atom can migrate between two deep basins with migration activation energies at 1.5 or 1.3 eV. Given the relatively large energy barrier at approximately 3.8 or 4.7 eV, escaping from the deep basin is difficult for the Si atom. This investigation showed that the number and distribution of ORS, namely, the adsorption site of hydrogen atoms and the removal site of surface hydrogen atoms, can affect the adsorption and migration of Si atoms on the hydrogen-terminated diamond surface. Electron structure analysis further reveals that the reactivity of the surface C atoms and the charge transfer amount between the Si and surface C atoms affect the adsorption and migration of Si atoms.

1. Introduction

Si-doped diamond films have attracted increasing research attention, particularly on the silicon vacancy (SiV) color center [1,2]. The SiV color center in diamond films can be formed simply through ion implantation techniques [3] or the addition of Si-containing gases in the process gas during diamond film deposition [4,5]. Results indicate that the SiV color center, which shows a strong luminescence with a zero phonon line (ZPL) at 738 nm, has a narrow ZPL (≈5 nm), weak vibronic sidebands, and a short (∼1 ns) lifetime at room temperature [2–5]. With these advantages, the SiV color center is a potential single-photon source. Si doping was also used to deposit smooth fine-grained diamond films [6,7]. Sun et al. reported that Si doping decreased the grain size and surface roughness of the films. Si-doped diamond-coated drills with smooth surface and favorable adhesive strength exhibited good wear resistance and excellent cutting performance [6]. The first Si addition in diamond film deposition was conducted to improve the film adhesion to substrates and prevent the catalytic effect of the substrate elements, such as iron-, cobalt-, and nickel-based materials [8]. Since 1992, Jiang et al. has been studying diamond/β-SiC composite films [8–13]. Using $Si(CH_3)_4$ tetramethylsilane as one of the precursor gases, the diamond/β-SiC composite gradient films were successfully synthesized. The competition between a kinetic product (diamond) and a thermodynamic product (β-SiC) was also investigated [9–13]. Moreover, the wettability of diamond/β-SiC composite thin films for biosensoric applications was studied [14]. Most studies on Si-doped diamond films show that film microstructure can be influenced by the process parameters. Therefore, our previous studies focused on the migration behavior and configuration evolution of Si-doped diamond films using first principles methods [15,16]. Results revealed that the Si atom diffusion on the clean diamond (001) surface is relatively easy and filling of Si on the vacancy defects in the deposition of diamond/Si composite film is possible, thereby probably improving the film compactness.

According to plasma field research [17], numerous hydrogen atoms exist on the substrate surface in a hydrogen-rich diamond deposition. As a result, the adsorption of hydrogen atoms and the abstraction of surface hydrogen atoms play an important role in the diamond growth [18]. Therefore, our present study focuses on the adsorption and migration behavior of Si atoms on a hydrogen-terminated diamond (001) surface. The investigation concentrates on a Si atom on a fully hydrogen-terminated surface and a Si atom on the hydrogen-terminated surface with one, two, and three open radical sites (ORS).

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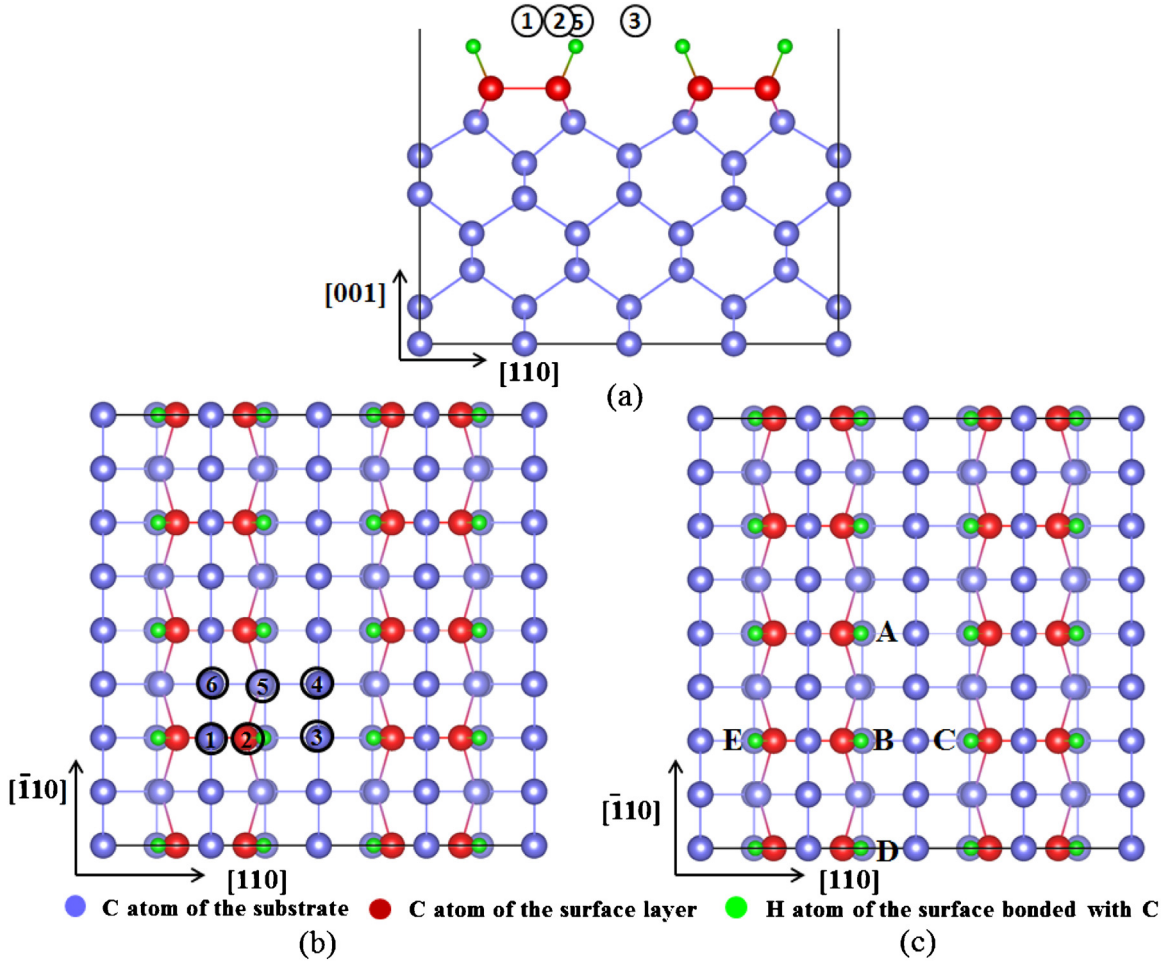

Fig. 1. Six highly symmetrical positions and open radical sites (ORS) on the reconstructed hydrogen-terminated diamond (001) slab: (a) main view and (b) top view. (c) ORS. When hydrogen atom B is abstracted, the configuration represents the model of a hydrogen-terminated diamond (001) slab with one ORS, denoted as 1ORS. When hydrogen atoms A and B are abstracted, the configuration stands for the model with two ORS along the dimer row, denoted as 2ORS-R. When hydrogen atoms B and C are abstracted, the configuration represents the model with two ORS along the dimer chain by the ring-opening side, denoted as 2ORS-CO. When hydrogen atoms E and B are abstracted, the configuration represents the model with two ORS along the dimer chain by the ring-closing side, denoted as 2ORS-CC. When hydrogen atoms A, B, and D are abstracted, the configuration represents the model with three ORS along the dimer row, denoted as 3ORS-R. When hydrogen atoms E, B, and C are abstracted, the configuration represents the model with three ORS along the dimer chain, denoted as 3ORS-C.

2. Calculation details

The calculation method was described in our previous study [19]. All calculations were carried out with a Vienna ab-initio simulation package (VASP) code [20–22], which was based on density functional theory. In the calculations, plane wave basis and periodic boundary conditions were utilized to calculate the Kohn–Sham ground state. The electronic and ionic interactions were represented with projector-augmented wave method [23,24]. Local density was described using the generalized gradient approximation based on the Perdew–Burke–Ernzerhof formulation [25,26]. During a self-consistent calculation to identify the electronic ground state, the Brillouin zone was sampled with the Monkhorst–Pack k-point grid [27]. A $5 \times 5 \times 1$ k-point mesh was used for slab calculations. Electron and ion relaxation convergence precisions were 10^{-4} and 10^{-3} eV. Moreover, spin-polarized calculations were conducted for the structure and configuration optimizations. The minimum migration energies of atoms on the diamond (001) surface were calculated with nudged elastic band (NEB) method in VASP [28].

To model the hydrogen-terminated diamond (001) film, a $4 \times 4 \times (8+1+8)$ slab composed of eight carbon layers with $(4 \times 4)16$ carbon atoms per layer, one hydrogen layer, and eight vacuum layers was used as shown in Fig. 1. The vacuum layer was approximately 0.802 nm to prevent periodically arranged interference.

Hydrogen-terminated diamond (001) film model was selected because of the abutment of hydrogen atoms on the surface in the diamond film synthesis [17]. During relaxation, the three bottom layers of C atoms were fixed, whereas the others moved freely. After relaxation, the hydrogen-terminated diamond (001) surface underwent reconstruction. The length of the dimer bond was 0.162 nm, and the bond length between hydrogen atoms and surface carbon was 0.102 nm.

Energies of a single Si atom and a single carbon atom were determined (Table 1) by fitting the calculated cohesive energy with the experimental value. The calculated cohesive energy and lattice constant agreed well with experimental values. Therefore, our calculations are reliable for investigating the adsorption and migration behavior in this system.

Adsorption and migration behavior of a Si atom on the hydrogen-terminated diamond (001) surface was studied. On the reconstruction surface of the hydrogen-terminated diamond (001), six highly symmetrical positions existed as shown in Fig. 1(a) and (b). The six positions were described in the previous study [19]. A single Si atom was set at each of the six positions to calculate