



Electronic structure and stability of hydrogen defects in diamond and boron doped diamond: A density functional theory study



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ABSTRACT

Isolated hydrogen and hydrogen pairs in bulk diamond matrix have been studied using density functional theory calculations. The electronic structure and stability of isolated and paired hydrogen defects are investigated at different possible lattice sites in pure diamond and boron doped diamond. Calculations revealed that isolated hydrogen defect is stable at bond center sites for pure diamond and bond center puckered site for boron doped diamond. In case of hydrogen pairs, H₂ defect (one hydrogen at bond center and second at anti-bonding site) is stable for pure diamond, while for boron doped diamond B–H_{2BC} complex (one H atom at the B–C bond centered puckered position and the other one at the puckered position of one of the C–C bond first neighbor of the B atom) is most stable. Multiple hydrogen trapping sites in boron doped diamond has also been studied. Calculated results are discussed and compared with previously reported theoretical results in detailed.

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1. Introduction

Diamond is a wide band gap semiconductor with exceptional physical and electronic properties [1–4]. Recent advances in the synthesis of single crystal diamond via chemical vapor deposition (CVD) have demonstrated that material with exceptional electronic and optical properties can now be produced, and this has enlivened interest in exploiting the extraordinary properties of diamond [5]. In particular, diamond exhibits very high electron (4500 cm² V⁻¹ s⁻¹) and hole (3800 cm² V⁻¹ s⁻¹) mobilities [5], breakdown strength (10⁷ V cm⁻¹) and thermal conductivity (>2000 W m⁻¹ K⁻¹) [6], which enable diamond to surpass other wide band gap materials for high power and high frequency electronic applications. However, the electronic properties of diamond are altered by defects and impurities grown into the material and introduced during the processing steps in device fabrication. Therefore, it needed to understand the electronic properties and lattice structures of defects or impurities in diamond matrix.

Hydrogen related defects play an important role in diamond and strongly affects the electronic and structural properties. Hydrogen is usually the most abundant element present in the CVD growth

environment of diamond and is used in many processing techniques. It is now established that under the appropriate conditions hydrogen can be readily incorporated into bulk diamond. Detailed information on the structure of hydrogen-related defects in diamond is an essential prerequisite for understanding the influence of hydrogen on electrical and optical properties, and ultimately exploiting the full potential of these materials. Furthermore, diamond is the ideal model wide band gap material for both experimental and theoretical investigations of hydrogen-intrinsic defect complexes.

Isolated hydrogen atom and hydrogen atom pairs in diamond matrix have been attracted researchers over the last decades. In last couples of years, the energies or stabilities of several sites for isolated hydrogen in diamond have been theoretically calculated using different theoretical approaches. Most of the theoretical calculations [7–10] predicted the bond center sites as a most stable geometry, although one semiempirical calculations suggested an off-axis sites to be more stable [11]. For H atom pairs, different geometries are proposed and reported in literature. Two nearby H atoms has been predicted to be more stable, when one carbon atom sits on bond center site and other on the same axis but on the other side of one bond center carbon atoms, which is called the anti-bonding site. The H atoms pairs is called H₂ defect. This geometry of H atom pairs is found highly unstable in Si and Ge semiconductors. Silverman et al. reported that the average hydrogen interstitial formation energy in the amorphous region is lower than the hydrogen interstitial formation energy in nano-diamond [12].

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Despite the basic interest of isolated H atom defect, H atom has been shown to neutralize the electrical activity of both n-type and p-type dopants and to produce a variety of defects and impurity states. This has been studied extensively more than twenty years in Si and Ge semiconductors [13,14]. In recently years, it has been noted that hydrogen can also passivate impurities in diamond [15,16]. In last few years, there has been intense theoretical activity on boron–hydrogen complex in diamond matrix [17–22]. The formation of boron–hydrogen or boron–deuterium complexes convert p-type boron doped sample into highly insulating sample as revealed by capacitance–voltage measurements [15] and hall measurement [23,24]. Other spectroscopic techniques Fourier transform Infrared [25] and cathodoluminescence measurements also confirm the passive nature of hydrogenated B-doped diamond [26]. It is also reported that excess hydrogen or deuterium plasma exposed B-doped layers shows the n-type conductivity with shallow activation energy (≈ 0.23 eV) [27–28], which has been very interesting topic in last few years [29]. This has been a controversial topic in theoretical calculations. Some density functional calculations support the experimental findings [20–21], whereas other calculations rule out the proposed explanation of n-type conductivity by the formation of boron–hydrogen (B–H) complex formation [17–19].

In this paper, we report on the electronic structure and stability for the isolated H atom and H atom pairs defects in pure diamond and boron doped diamond are studied by means of density functional theory (DFT) using plane wave method. Different possible geometries are studied and a comprehensive view of isolated H defect and H atom pairs defects is reported. The main objective of this work is to present detailed ab initio calculations of the total energy, structure optimization and densities of states (DOS) for the H related defect diamond matrix in different possible geometries. All the calculations have been done by using supercell technique. To reduce the possible errors due to calculation parameters we have used the large cell and large set of k-points. Calculation details are discussed in brief in Section 2, Theoretical calculation for hydrogen defect in pure diamond are given in Section 3 and H defect in B-doped diamond are described in Section 4.

2. Calculation details

The electronic structure and stability of isolated hydrogen and hydrogen atom pairs complexes were investigated using the Vienna Ab-initio Simulation Package (VASP) code [30]. It is based on DFT within the generalized gradient approximation (GGA) [31]. Projector Augmented wave is used with a basis cutoff equal to 318.6 eV [32]. The Monkhorst–Pack scheme [33] with $5 \times 5 \times 5$ k points has been used for integration in the Brillouin zone. The error of total energy convergence is less than 10^{-4} eV. Tetrahedron method with Blochl corrections have been used to calculate the densities of states. The calculation of the energy band gap for pure diamond ($E_g = 4.2$ eV) is in good agreement with theoretical calculations [9,11,34]. To generate a puckered position, the hydrogen atom was initially displaced by a small distance off-axis and the whole cell was allowed to relax.

Fig. 1 shows the schematic of the selected sites of hydrogen atoms in diamond cell. Carbon atoms are shown by gold circles as a diamond cell. The hydrogen atoms at different interstitial sites are shown by black circles. The tetrahedral (T) site lies equidistant from four carbon sites and possesses T_d symmetry, the hexagonal (H) site lies midway between two T sites and possesses D_{3d} symmetry. The bond-centered (BC) site is the mid-point between two atom sites (D_{3d} symmetry) and anti-bonded (AB) configuration is opposite the BC site along the same axis, possesses C_{3v} symmetry [13].

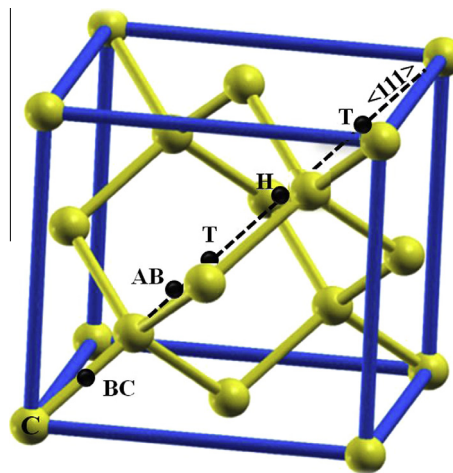


Fig. 1. Schematics of the possible hydrogen sites in diamond cell. Carbon atoms are shown as golden circles and hydrogen atoms by black circle. The tetrahedral (T) site lies equidistant from four carbon atoms and the hexagonal (H) site lies midway between two T sites. The bond-center (BC) site is the midway between two carbon atom sites and anti-bonded (AB) sites is opposite the bond center site along the C–C axis as showing in figure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Hydrogen in pure diamond

3.1. Isolated hydrogen in pure diamond

For isolated H atom, there are mainly three different sites namely; bond-center (BC), tetrahedral (T), and hexagonal (H) site. We performed the calculations for all the three possible sites of isolated hydrogen in diamond matrix. Fig. 2 shows the relaxed structures of hydrogen at (a) bond-centered, (b) tetrahedral (T) and (c) hexagonal site. Total energy calculations show that the bond-centers site is the most stable one. For this configuration H atom sits at equidistant from both carbon atoms with 1.14 Å C–H bond lengths. The observed C–H bond length for H at bond center is higher than the previously reported value. The higher bond length could be possible due to full relaxation and use of bigger size supercell in present study. In the present study, the bond lengths and bond angles are mentioned within the error bar of ± 0.01 Å and $\pm 0.1^\circ$, respectively.

Some earlier calculations using the ab initio Hartree–Fock (HF) approach reported the tetrahedral interstitial site (T) is a deep minimum of the total energy [35–37]. Bond-centered (BC) site was also found more stable compare to the tetrahedral interstitial site (T) using basis-set ab initio HF [7,38,39] and later by DFT calculations [8]. In early stage, Estreicher et al. [37] predicted the T site as a most stable but later in fully relaxed cluster, they also reported BC site as a most stable site for isolated hydrogen. Tachikawas also discussed the electronic states of hydrogen atom trapped in diamond using cluster model calculations and predicted that the tetrahedral site is most favored site for H trapping in diamond matrix. He calculated the C–C bond length was slightly elongated by the insertion of hydrogen atom in diamond lattice [40]. A very different site off-bond axis was also reported to be the lowest energy position that an H atom occupies in diamond. It is a 6 fold degenerate site with respect to the C–C bond, which is denoted by “Equilateral Triangle” ET site [11]. This site was not reproduced by the others. Single H at anti-bonding (AB) site was also calculated, which is highly unstable compared to bond-center and tetrahedral sites [41].

For most stable bond center site, the C–H bond length is 1.14 Å for both the nearest carbon atoms. The observed C–H bond length is good agreement with reported C–H bond length in range of

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