



Theoretical study of migration processes in bulk diamond

B. Butorac*, A. Mainwood

Physics Department, King's College London, Strand, London WC2R 2LS, UK

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ABSTRACT

A large number of complex defects are seen in natural and synthetic diamonds, but it is not known whether they form during growth or as a result of later processes. An understanding of diffusion profiles of the dopant impurities is crucial for design of electronic devices. We present here theoretical work on migration processes for several complexes including N, H and vacancies in diamond, to find out how they form. First-principles density functional calculations have been performed to study structural properties and the activation energies for migration of these defects. Migration paths were derived by constructing a set of several intermediate structures between two energy minima by linear interpolation. The effect of temperature on calculated barriers is described by including vibrational energy and entropy. It was found that the energy barrier for migration of interstitial hydrogen between two bond-centred positions is 2.8 eV. Also, hydrogen is readily trapped by both vacancies and by the N–V complex. Energies liberated in these reactions are 5.5 eV and 5.8 eV respectively.

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1. Introduction

The development of diamond-film growth techniques has stimulated an interest in the use of diamond as a semiconductor in electronic devices. Possible applications include those that require high-temperature, high-power, high-frequency and irradiation tolerance. These properties come from diamond's high thermal conductivity, high carrier mobility and high breakdown field. But pure diamond with an indirect band gap of 5.5 eV is a good insulator and practically useless as a semiconductor. So in order to create these electronic devices it is necessary to dope diamond with donor or acceptor impurities. Atomic migration is quite an important process in solids. The diffusion of impurities in doped diamond can play a central role in the fabrication of electronic devices. If the dopants themselves are mobile, they may migrate out of the desired regions under processing conditions, or other mobile defects may be trapped by the dopants passivating them. Alternatively the diffusion of impurities may be exploited in order to grow the dopant profiles required.

This paper reports on a study of migration processes in bulk diamond. It is arranged as follows. In Section 2, we describe methods used in the calculations. In Sections 3, 4 and 5 we summarize results obtained for the diffusion of bond-centred (BC) hydrogen, vacancy and hydrogen related complexes and N–V–H defect. In Section 6 we briefly report on the stability of the defects investigated and conclude in Section 7.

2. Computational method

Selfconsistent density functional theory (DFT) calculations using SIESTA [1] software were carried out. This code utilises localised atomic

numerical basis set and periodic boundary conditions to describe valence electrons. Core electrons are treated by norm-conserving pseudopotentials which are constructed in the Troullier–Martins scheme [2]. In our calculations the DZP (double zeta plus polarisation orbitals) basis set was used to represent valence electrons. Generalised gradient approximation (GGA) was employed for the exchange–correlation potential. In particular, we used the Perdew–Burke–Ernzerhof (PBE) parameterisation of the exchange–correlation functional [3]. One (Gamma) k-point was used in simulations and an energy cutoff of 350 Ry. Bulk diamond was represented with the 64-atom cubic supercell with the side length of $2a_0$.

In principle, we can't be sure that the obtained relaxed structures are indeed global minima. However, by obtaining very similar total energies when end-point structures are totally equivalent (differences are up to 0.01 eV), we can reasonably assume that relaxed structures are good representations of ground states.

Calculation of migration barriers was performed in the same manner as in [4]. First, for each complex a relaxed structure is obtained by using the conjugate gradient procedure. Since impurities tend to change the lattice constant, the volume of the supercell was not fixed while we were finding global minima. Once minimum energy structures have been obtained, a set of several intermediate structures between the initial and final step are generated along the reaction path by linear interpolation. This is done in order to calculate the minimum energy path for a diffusion mechanism. In each of the intermediate structures the impurity atoms were not allowed to move nor were the carbon atoms in the outermost part of the supercell. The rest of the atoms could move freely until the forces on them vanished in order to optimize the energy at each stage.

It should be noted that barriers obtained in this way give an upper estimate of the real barriers due to the stress induced in the supercell by fixing the outermost atoms.

* Corresponding author. Tel.: +44 2078482836.

E-mail address: bozidar.butorac@kcl.ac.uk (B. Butorac).

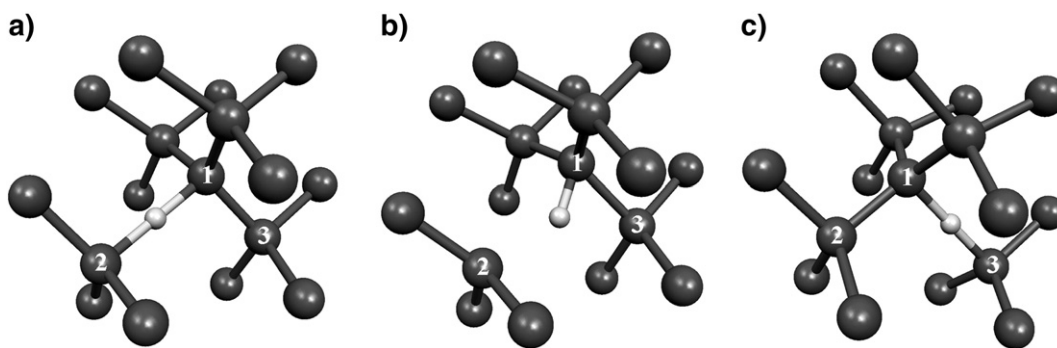


Fig. 1. Structural configurations along the reaction path for a hydrogen migration between two equivalent C–H–C structures.

The barriers given in Sections 3, 4 and 5 describe 0 K temperature barriers, since we only took into account the internal energy U_{int} . The correct quantity to be used to compare with experiments is Gibbs free energy G , not the internal energy.

$$G = U - TS + pV - \sum_i \mu_i N_i \quad (1)$$

U is the total energy of the system and is equal to the sum of the internal energy U_{int} and the vibrational energy U_{vib} . T is the temperature and S is the entropy. The entropy consists of the configurational, the electron-hole pair and the vibrational part. The dominant contribution is from vibrations and that term was only considered. The expressions for U_{vib} and S_{vib} can be found in [5, 6]. pV term is usually neglected since the solid system is relatively incompressible so is assumed to be at constant volume. μ_i is a chemical potential of a certain species and N_i is a number of particles. The last term is taken into account only if the number of particles changes. In order to obtain U_{vib} and S it is necessary to calculate vibrational frequencies. They can be derived by diagonalizing the dynamical matrix, but this task is particularly time consuming. In our analysis we obtained the complete dynamical matrices for the supercells used. Taking into account both U_{vib} and S_{vib} gives a more physical picture of the migration processes since different structures along the migration path have different vibrational spectra, so their contributions to U_{vib} and S_{vib} will differ. This approach is described in [5].

We should also mention that the calculated dynamical matrices at our estimates of saddle points showed that these estimates are indeed good approximations of the saddle points. We deduced this by looking at the phonon frequencies calculated from the dynamical matrices which showed that there was a maximum in the direction of the migration path, but minima in all other co-ordinates.

All defects were analysed in the neutral charge state. The lines on all figures are to guide the eye.

3. Interstitial hydrogen

The hydrogen atom was placed at the bond-centred (BC) interstitial position between two carbon atoms. This initial structure has C_{2h} symmetry. After relaxation the defect retains this symmetry and the H atom stays at practically the same position while the two nearest C atoms move away from hydrogen so that the C–C bond is dilated to 2.31 Å. This is 48% larger than in the pure diamond. This defect is quite localised since displacements of the atoms from the second shell are less than 4%. The relaxed structure is shown in Fig. 1. The bond lengths are C₁–H 1.15 Å and C₂–H 1.15 Å, while the angle C₁–H–C₂ is 180° in the minimum energy structure. This is in a good agreement with results summarised in [7]. We investigated the energy barrier for the process in which H atom migrates between two equivalent bond-centred positions (BC → BC). The path is shown in Fig. 1 and the barrier in Fig. 2.

During migration the bond between H and its carbon neighbour labelled as C₂ is broken. The values obtained by other authors are

1.8 eV [8], 1.9 eV [9], 2.14 eV [10] and 2.6 eV [11], so our result is just above the highest value.

To justify the neglect of tunnelling we have investigated the tunnelling probability for a similar barrier to that calculated for H. A smooth, curved barrier, like Gaussian shaped one, can be approximated as a juxtaposition of square barriers. In the limit of infinitely narrow barriers, the expression for tunnelling probability becomes [12]:

$$|T|^2 \approx e^{-2 \int dx \sqrt{(2m/\hbar^2)(V(x) - E)}} \quad (2)$$

with the integration over the region in which the square root is real, where m is the mass of the particle, in this case it is the mass of the hydrogen atom, and E is the particle energy. When we put all the data together for our particular case, taking the energy of the particle to be half of the barrier height, the transition probability is about 0.09. Since this is relatively small, it is possible in the first approximation to neglect tunnelling effects.

The phonon density of states (PDOS) was calculated for a supercell containing bond-centred hydrogen for a minimum energy structure and at the saddle point. There is a local vibrational mode due to the bond-centred hydrogen at 2825 cm⁻¹. This is in a good agreement with the value of 2919 cm⁻¹ in [8].

If we take into account U_{vib} and S_{vib} then the height of the barrier drops from 2.8 eV to 2.6 eV at 0 K, which is the same as in [11]. However, the free-energy difference between the saddle point and the ground state increases with temperature. The activation energy increases from 2.6 eV at 0 K up to 3 eV at 2000 K. Although the activation energy

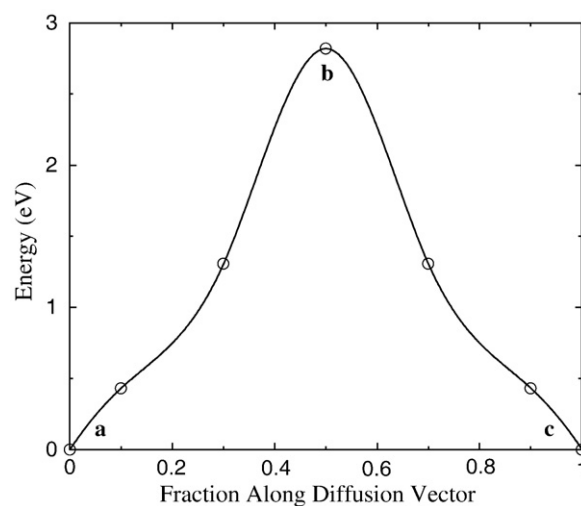


Fig. 2. The 0 K energy evolution along the reaction path during the process in which hydrogen migrates between two equivalent bond-centred positions (a and c) through the saddle point (b). The distance between the initial and final positions of the H atom is 1.25 Å.

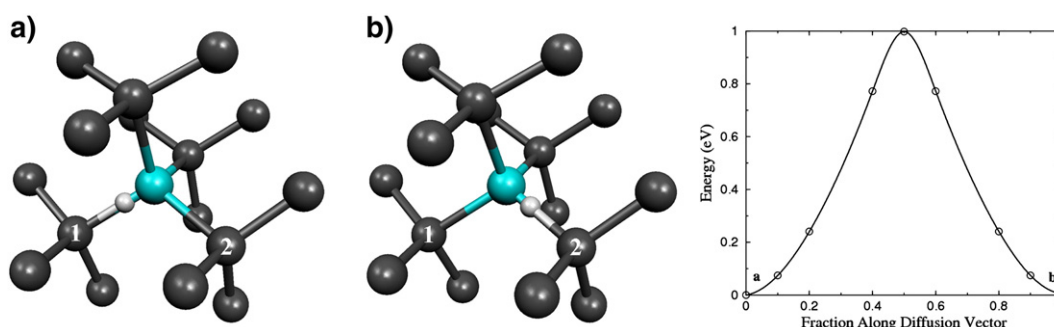


Fig. 3. Relaxed structures for V-H complex. Right: The 0 K barrier for the process when H migrates between two equivalent V-H structures (designated as a and b). The distance between the initial and final positions of H atom is 1 Å. Vacancy is represented as a light blue ball. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

increases with temperature, the probability of diffusion will still increase. This can be seen if we make an Arrhenius plot which displays the logarithm of diffusivity plotted against inverse temperature.

4. Vacancy and hydrogen related complexes

The hydrogen atom was placed halfway between the vacancy and one of the nearest C atoms along the [111] direction to make V-H complex. We also investigated the barrier for the process when H diffuses between two equivalent V-H structures. Relaxed V-H and the diffusion barrier we obtained are shown in Fig. 3.

Ab initio calculations of the hyperfine parameters for negatively charged V-H complex were performed in [13], to compare static defect models and the one which allows for the quantum tunnelling of hydrogen. They found that static models are inconsistent with experimental EPR data and that quantum dynamical models are in a good agreement with experiments.

Using Eq. (2), the tunnelling probability is found to be 0.26, so tunnelling of hydrogen atom can't be neglected in this case.

If we take into account U_{vib} and S_{vib} then the height of the barrier drops from 1 eV to 0.8 eV at 0 K. The free-energy difference between the saddle point and the ground state increases with temperature. The activation energy increases from 0.8 eV at 0 K up to 0.9 eV at 2000 K.

We continued by finding relaxed structures for two more defects, namely the one for which the H atom is between the first and second coordination site from the vacancy (V-C-H) and the one where H atom is between the second and third coordination site from the vacancy (which is accordingly defined as V-C-C-H). Also, the migration of H atom from V-C-C-H to V-H structure was analyzed

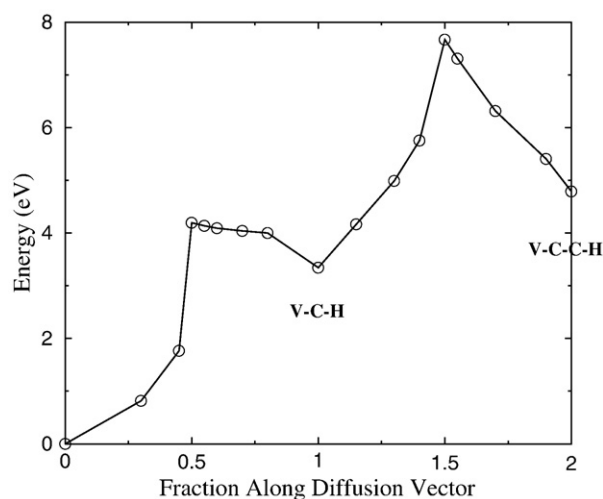


Fig. 4. The migration of hydrogen from V-C-C-H, which corresponds to coordinate 2, through V-C-H, which is located at 1, towards V-H which is at 0.

by obtaining the potential energy curve which describes the interaction between H and vacancy as a function of H position.

The capture of the hydrogen by the vacancy from V-C-C-H to V-H structure is shown in Fig. 4.

From Fig. 3, there is an obvious tendency for hydrogen to be captured by the vacancy, with the saddle points of 2.9 eV and 0.8 eV through intermediate structures.

5. N-V-H complex

Nitrogen is the most common impurity in diamond. A lot of work, both theoretically and experimentally has been done on nitrogen related defects in diamond. In natural stones, it usually appears in the form of the nearest neighbour pairs (A aggregates), but in most synthetic diamonds, it is present as single substitutional atoms (C centre). EPR experiments performed on single-crystal CVD diamond doped with ^{15}N showed that there is an important defect in these films [14]. It was suggested that this defect has C_{3v} symmetry and consists of hydrogen trapped at the N-V centre, with hydrogen bonded directly to nitrogen. Goss et al. [15] showed that local density functional theory, when the H nuclei are treated classically, does not support this model and that H atom actually makes a bond with a carbon neighbour of the vacancy. They suggested that the experimentally observed symmetry could be explained by the quantum tunnelling of the H atom between three equivalent C sites. Shaw et al. [13] treated the hydrogen nucleus quantum mechanically and found that the hyperfine parameters of the dynamical model, which accounts for H tunnelling, are in good agreement with EPR data.

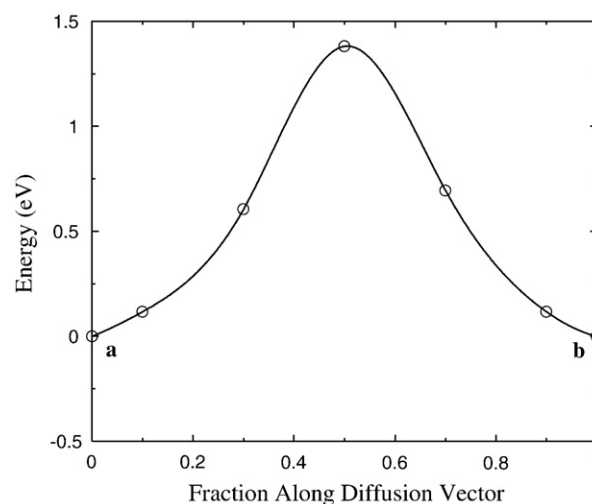


Fig. 5. The 0 K energy evolution along the reaction path during the process in which hydrogen migrates between two equivalent N-V-H structures. The distance between the initial (a) and final (b) positions of the H atom is 1 Å.

In this section we deal with the defect consisting of N–V with H, which we shall denote as N–V–H.

First we created N–V complex and found that energy needed for N and V to interchange is 4.8 eV while the dissociation barrier is 3.9 eV. The barrier for N and nearby V to form N–V is only 0.4 eV. After having obtained the ground state for N–V complex, H atom was placed halfway between the vacancy and one of the nearest carbon atoms along the [111] direction. After relaxation, the structure obtained is in agreement with the model described in [15].

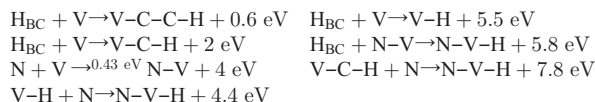
We found a local minimum when the H atom is bonded directly to the N, but this structure is 1.84 eV higher in energy than N–V–H system (close to 1.56 eV in [15]). N–H bond is 1.11 Å and is along [111] direction.

The energy barrier for diffusion of hydrogen between two equivalent N–V–H structures is found to be 1.4 eV and is given in Fig. 5. This suggests that H atom is static and could not easily hop amongst three equivalent structures, in contradiction with results in [13] and [14]. However, using Eq. (2) again, the tunnelling probability is found to be 0.2, which is quite high and allows for quantum tunnelling of hydrogen atom through the barrier in agreement with [13].

If we take into account U_{vib} and S_{vib} then the height of the barrier drops from 1.4 eV to 1.1 eV at 0 K, which would further increase the tunnelling probability. The free-energy difference between the ground state and the saddle point slightly decreases as a function of temperature and is equal to 1 eV at 1300 K.

6. Stability of defects

Using total energies obtained for minimum energy structures of all defects and methodology as in [16], we were able to tell something about their stability. Binding energies were estimated for several reactions:



We can see that hydrogen is readily trapped by the vacancy. The value of 5.5 eV is quite lower than 8.4 eV obtained in [17]. However, for example, it should be noted that it was calculated in [17] that boron–boron aggregate is 2.09 eV more stable than two isolated substitutional boron atoms and Goss and Briddon [18] obtained only 0.8 eV. $\text{C}_{44}\text{H}_{42}$ cluster was used in [17] and 64–216 atom supercells were employed in [18]. So, it is possible that the size of the cluster might have the effect on results in [17]. Also, vacancy is easily trapped by the nitrogen and the energy gain is 4 eV which is somewhat lower than 4.7 eV in [16] and higher than 3.5 eV in [19]. Since our value of binding energy of N–V is in between results from [16] and [19], we can assume that it presents a reasonable estimate of binding energy as well as the values in other equations. Therefore, the value of 8.4 eV in [17], for a stability of V–H complex could be an overestimation. We can also see that V–H and N–V–H systems are energetically favourable.

7. Conclusions

Ab initio calculations were performed to study migration paths of hydrogen in several complexes. It was found that the barrier for hydrogen to migrate between two bond-centred positions is 2.8 eV. However, when zero point energy is included, this barrier is reduced to 2.6 eV at 0 K. The activation energy for migration between two equivalent V–H structures is 1 eV. The diffusion profile for H migration from V–C–H to V–H structures shows that V–C–H is 4.8 eV and V–C–H is 3.3 eV higher in energy than V–H. The barrier for H to go from V–C–H to V–H is 2.9 eV while the barrier for H to go from V–C–H to V–H is 0.8 eV. So, we can see that it is energetically favourable for H to be trapped by the vacancy.

We also studied hydrogen aggregation with N–V defects and found that hydrogen is readily captured by this defect. Energy gained in reaction $\text{H}_{\text{BC}} + (\text{N-V}) \rightarrow (\text{N-V-H})^0$ is substantial and amounts for 5.8 eV. The barrier for H to migrate between two equivalent N–V–H structures is 1.4 eV.

Although the values obtained for migration of H atom in V–H and N–V–H structures suggest that H atom would be static at room temperatures, calculation of tunnelling probabilities reveals the quantum nature of hydrogen atom. In favour of this is the decrease of barriers when zero point energy is taken into account, which further increases the tunnelling probability.

Acknowledgments

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