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HYDROGEN BONDING IN DIAMOND: A COMPUTATIONAL STUDY

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We present tight binding molecular dynamics simulations of the diffusion and bonding of hydrogen in bulk diamond. The motion of hydrogen atoms and the resultant structural and electronic energy level changes are investigated. The hydrogen atoms were found to have a tendency to migrate to the surface layer of diamond, resulting in a local deformation of the lattice, creating new energy states above and below the Fermi energy in the bandgap of the diamond density of states. In the diamond bulk, at high hydrogen concentrations, vacancies created by a hydrogen atom are quickly filled with other hydrogen atoms causing a deformation of the diamond lattice, inducing H₂ formation. This creates new energy states above the Fermi energy and reduces the secondary bandgap of the diamond density of states.

Keywords: computer simulation; diamond; hydrogen

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1. Introduction

As well as being decorative, diamond is a material of technological importance. Applications include electronic devices such as diamond cold cathode emission displays, piezoelectric effect devices as well as other semiconductor applications. Whether the diamond phase of carbon is natural or polycrystalline CVD (chemical vapor deposition) grown¹ it is always contaminated with hydrogen (H). Hydrogen impurities

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affect the physical properties² and passivate electrically active defects³.

Experimental evidence for the presence and effect of the hydrogen on diamond crystal has been obtained from many studies using complementary techniques. Nanocrystalline diamond films obtained by plasma deposition were reported to have a large H content in the films, with diamond crystallites of ~ 5 nm in diameter^{4,5}. SIMS (Secondary Ion Mass Spectroscopy), NEXAFS (Near-Edge X-Ray Absorption Fine Structure), high-resolution transmission electron microscopy, x-ray spectroscopy and many other techniques are widely used in order to study these intriguing crystallites. Ion NEXAFS performed on hydrogenated diamond surface show a clear energy peak which is associated with a transition of a carbon 1s electron to a σ^* bond of the carbon and a hydrogen atom⁶. It is of great interest to determine whether this can be associated with electronic states in the band gap which are created due to the H bonding on the surface of the crystal.

Despite the use of highly advanced experimental techniques, microscopic description of the motion, assignment and the electrical effect of H in diamond remains elusive. However, in simulations, specific atomic configurations can be examined in detail. Clarification of the differences between different microstructures could lead to the formation of new structures and new insights on the role of H in the formation of nanocrystalline diamond films.

The behavior of H in diamonds has been simulated using various computational techniques^{7,8} in order to understand the binding and diffusion pathways for atomic

hydrogen in diamond. In contrast to semiempirical⁷ and first principle⁸ calculations, where only the relaxation of the hydrogen atoms inserted into several interstitial sites was studied, Saada *et al.*² used tight binding molecular dynamics to follow the dynamics of the H atom. They found that the lowest energy state H occupies is the Equilateral Triangle (ET) site. This degenerate site was identified experimentally with the anomalous muonium (Mu*) site in diamond⁹. Although this result is not confirmed by static ab initio computations, strong experimental evidence suggests that just as for bandgap estimation tight-binding MD may provide a better description here, than the so called “ab initio” method which despite its name also includes approximations.

In our present study, various amounts of hydrogen atoms diffusing into numerous different lattice structures (including amorphous carbon regions) were simulated. As the concentration of the H in the diamond bulk was increased to $\sim 10\%$ we found new symmetries of H atoms in the diamond. The H atoms contributed new energy states, above and below the Fermi level, as well as reducing the secondary bandgap in the diamond conduction band. We used tight-binding molecular dynamics simulations focusing on the changes in electronic and chemical structures due to the migration of H in diamond. In the next section we describe the computational models and the details of our sample preparation. In section 3 we give the results of our simulation. Finally, in section 4, we present our conclusions.

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2. Details of the simulation

Our simulations were made with a canonical ensemble (NVT) and a tight-binding (TB) based model¹⁰. The tight binding scheme incorporates electronic structure calculations through an empirical tight-binding Hamiltonian, bridging the gap between *ab-initio* calculations, which are capable of modelling only a small number of atoms, and calculating with empirical classical potentials which may have problems of accuracy¹¹. We used OXON, a tight-binding code¹¹ which is made self-consistent by the use of local charge neutrality, which is appropriate for hydrogen and carbon based systems where negligible charge transfer take place. The TB parameters selected were shown to have good agreement with *ab-initio* calculations and various experiments¹¹. The present model has been shown to be transferable to environments outside those included in the TB parameter fitting, such as hydrocarbon molecules, diamond surfaces and amorphous diamond-like carbons^{11,12}. We carried out Molecular dynamics (meaning solving Newton's equations of motion) to observe the diffusion of hydrogen atoms and the formation of H₂ molecules in diamond. All samples were observed interactively with AViz¹⁵ and in interesting cases measurements and statistics were gathered.

Various samples were created to study the effects of the diffusion of H atom(s). Each sample was designed to explore different aspects of the diffusion and therefore each sample differed by one or more of the following characteristics: sample size, boundary conditions and number of hydrogen atoms simulated in the sample. In

some, the temperature was also varied. Most samples were initially arranged as perfect cubic diamond crystals of 64 carbon atoms, with edges of 7.11Å. The effect of the sample size was also checked with a cubic 216 carbon atom sample with 10.665Å edges. The results achieved from the large supercell yielded quantitatively the same results as those with the small supercell, justifying the use of the small supercell for the remaining studies to economize on computer resources. The initial density of the samples was $\rho = 3.55\text{g/cm}^3$. Unless stated otherwise, we considered initially the T_d interstitial site for hydrogen in diamond, which is known to be a high energy interstitial site^{8,2,14}. All atoms were allowed to relax by the conjugate gradient algorithm, and in most cases, periodic boundary conditions were applied in all three directions and the temperature was simulated to be 500°K over a period of 20-32ps (after equilibrium was achieved).

The total CPU (central processing unit) time used for the simulations was approximately 10 processor weeks, this corresponds to a ~two day run per simulation (which corresponds to ~20ps of simulated time), on a dual 1.8GHz Xeon server running RedHat Linux.

3. Results

Selected simulations which exhibited particularly interesting phenomena are now described;

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3.1. One and two hydrogen atoms

As found previously by Saada *et al.*², in a sample of 64 carbon atoms with one hydrogen atom, the sample entered a configuration where the H atom oscillated between six ET sites (for a complete description see Saada *et al.*²). The H was found to take a position two-thirds of the distance between adjacent diamond hexagonal planes. In the DOS plot, a new state of $\sim 0.5\text{eV}$ above the middle of the energy gap appears due to the H interstitial at the ET site and a creation of the dangling bond.²

When the periodic boundary condition along one axis was broken (by doing so, a vacuum is simulated), we found that the system of the 64 atom sample rapidly enters a configuration where the hydrogen atom is located on the C-C bond of the outer layer of the diamond sample, causing the outer-most carbon to shift, forming a 1.0\AA bond with the inner carbon, on the surface of the diamond. On computing the DOS we found that new states are created in the diamond bandgap above the Fermi level.

A similar configuration was observed in a different sample arranged with three layers, containing a total of 144 carbon atoms. The first and second layers of this sample were arranged as a diamond lattice and the third as vacuum (containing no atoms), the interlayer distance being 3.55\AA . In the first layer (bulk-like) the atoms

were frozen and in the second layer the atoms were free-to-move. In this sample, periodic boundary conditions were applied in all directions. First, a single hydrogen atom was implanted at the T_d site in the free-to-move region, and was simulated for 10ps at 500°K. The hydrogen quickly diffused to the surface of the diamond lattice, near the vacuum region, causing a dislocation of an outer-most carbon atom, forming a carbon vacancy. The hydrogen diffused to this vacancy, bonding to the inner carbon atom, with a bond length of $\sim 1.0\text{\AA}$ (the same as for the sample with the broken boundary condition). Then a second hydrogen atom was implanted at the same site as the first, this hydrogen diffused to the vacancy already created, pairing with a carbon atom creating a C-H-H-C complex with a bond length of $\sim 1.0\text{\AA}$.

The DOS of the two samples (one with a broken boundary condition, the other with a semi-frozen lattice) are almost identical, revealing close relationships between different geometrical structures and preparation processes. New states are formed in the bandgap above the Fermi level (see Fig. 1). In an ion NEXAFS experiment⁶ with a surface sensitive mode performed on hydrogenated diamond surface, a photon energy peak of 287.5eV is observed, which had been previously assigned to a $C(1s) \rightarrow \sigma^*(C-H)$ transition, and therefore associated with the presence of C-H species on the diamond surface. This experimental result can be strongly correlated with our simulations: (i) the simulations show - there is a tendency of hydrogen atoms to migrate to the surface layer of the diamond creating a C-H complex. (ii) The 287.5eV peak (a $\sim 1.7\text{eV}$ difference from the bulk exciton) observed experi-

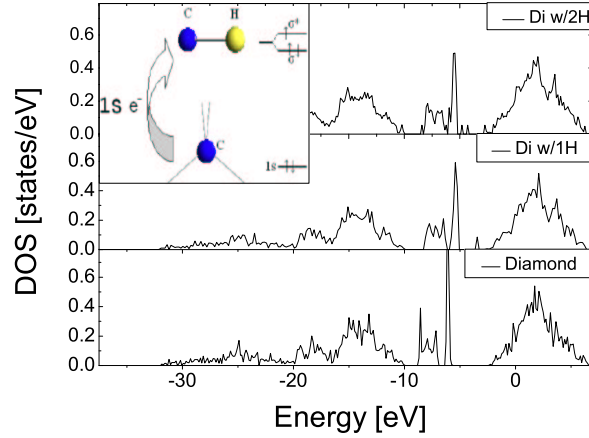
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Fig. 1. From top to bottom, density of states (DOS) of diamond with 2 H and 1 H at the surface, and without H (all with free boundary conditions). In the inset, we graphically show the $C(1s) \rightarrow \sigma^*(C-H)$ transition.

mentally could be associated with the simulated DOS which has a peak (caused by the H at the surface) at 1.9eV from the Fermi energy of the lattice.

3.2. H_2 molecule

Hydrogen molecules (H_2) were simulated in a cubic diamond crystal of 64 carbon atoms. In one sample, the hydrogen molecule was initially placed with one atom at the T_d site and the other at the distance of the hydrogen bond, i.e. 0.7\AA away. In a second case, the H_2 molecules were placed at a slightly smaller distance of 0.6\AA from each other (as suggested by Estreicher et al.⁸), to examine differences. Simulations were performed with the H_2 oriented in turn in the $x-y$, $y-z$ and $x-z$ planes to check directional dependence. The results of all these simulations were

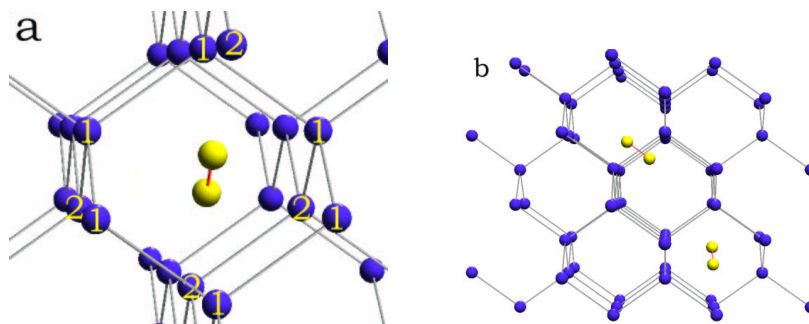


Fig. 2. The hydrogen atoms are colored white (light yellow in a color print) and the carbon atoms black (dark blue in a colorprint). a. H_2 symmetric location in a diamond sample with its 1^{st} and 2^{nd} nearest neighbor atoms numbered 1 and 2, respectively. b. $\langle \bar{1}10 \rangle$ view of two H_2 molecules displaced 3.32\AA apart.

the same to a good degree of approximation, thus showing that neither the distance between atoms nor the orientation of the molecule had an effect on the final result. In all cases the molecule was found to be oriented in complete symmetry with the diamond lattice, perpendicular to the $\langle 110 \rangle$ direction of the diamond lattice (see Fig. 2a). The average H-H bond length was $\sim 0.72\text{\AA}$ throughout the simulation. The distances between the center of the H-H bond to the first and second nearest carbon neighbors was calculated to be 1.47\AA and 2.30\AA (dotted and dashed lines in Fig. 2a). The H_2 bond created an angle with the diamond $\langle \bar{2}\bar{2}1 \rangle$ plane of 70.3° , and with the adjacent plane $\langle 2\bar{2}1 \rangle$ of 27.8° .

A different sample was prepared with 2 H_2 molecules implanted in the sample, displaced initially by a distance of 3.06\AA measured between the H-H bond centers. After a 20ps simulation, the molecules rearranged themselves so that the bond vectors were perpendicular one to another, despite the 3.32\AA between them (see Fig.

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2b). Each H_2 has preserved its H-H bond of $\sim 0.7\text{\AA}$ and each is located in complete symmetry with the diamond lattice as for a single H_2 .

3.3. 6 Hydrogen atoms

Six hydrogen atoms were implanted in a diamond sample of 64 carbon atoms with periodic boundary conditions. The hydrogen atoms were initially distanced $\sim 0.9 - 4.8\text{\AA}$ from each other. Due to the rapid migration of 2 hydrogen atoms to adjacent ET sites, creating two carbon dangling bonds, 2 additional hydrogen migrated to these carbon atoms. This created a scenerio where 4 of the hydrogen atoms were found to be in surrounding ET sites creating a cavity in the diamond lattice. This cavity was quickly filled with the remaining unbonded hydrogen atoms. These two remaining hydrogen atoms formed a hydrogen molecule due to the gap caused by the C-H complexes (see Fig. 3). The final distance between the 4 hydrogen atoms was $\sim 1.2 - 2.3\text{\AA}$. The electronic density of states (DOS) of this sample, shows new states which emerge in the diamond bandgap below the Fermi level (see Fig. 4).

4. Discussion and Conclusions

We applied the molecular dynamics scheme with a tight-binding Hamiltonian to samples with different geometries and boundary conditions to explain phenomena

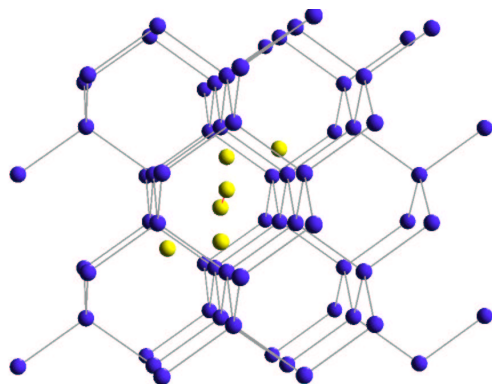


Fig. 3. $\langle 1\bar{1}0 \rangle$ view of a diamond lattice with 6 H atoms. Dark and light spheres are carbon and hydrogen atoms, respectively, and the grey lines represent nearest neighbor bonds.

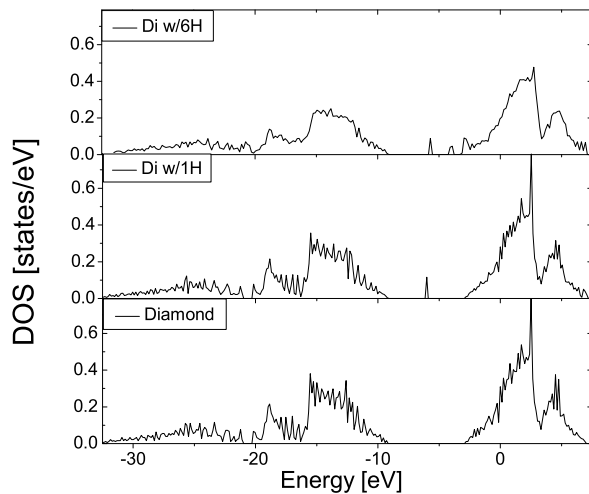


Fig. 4. Density of states (DOS) of diamond with 6 hydrogen atoms, with a single hydrogen atom and bulk diamond

of hydrogen bonding in diamond. A single hydrogen atom was found to form a C-H bond with one carbon, resulting in the breaking and stretching of other C-C bonds. The resultant bond structure can be correlated with a sp^3 hybridized C-H bond. This result has been previously observed in a SWNT¹⁶ (Single-Walled

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Nano-Tube), where hydrogen adsorption was found to expand the diameter of the nanotube hence, the C-C bond length enlarged in the vicinity of the C-H bond created, enhancing the sp^3 rehybridization.

Hydrogen atoms were found to have a tendency to diffuse to the surface layer of the diamond sample, as experimentally seen in SIMS measurements⁴, as well as in ion NEXAFS measurements. The $C(1s) \rightarrow \sigma^*(C-H)$ transition observed in the NEXAFS of ref.⁶, can be correlated to our calculated (simulated) DOS. In addition to this experimental evidence, this result can also be correlated to a half coverage exohydrogenated (8,0) SWNT. Calculations¹⁷ reveal a deformation of the cylindrical nanotube to become a rectangle with a diamond-like carbon at each corner. The hydrogens were found to contribute new energy states at the Fermi level of the DOS resulting in a DOS plot very similar to our calculations of the hydrogen on the surface of diamond (see Fig. 1).

The sites of hydrogen dimers were shown to have complete symmetry with the diamond lattice (see Fig. 2a), which is consistent with previous ab-initio calculations⁸. Two hydrogen dimers in the sample were found to form a perpendicular orientational order similar to the ground state (lowest energy) of molecular solid H_2 ¹⁸. This phenomenon, usually observed in a low-temperature high-pressure environment, occurs when the molecular orbitals (or the axes of quantization of the molecular angular momenta) orient along the body diagonals. The carbon lattice provides local pressure on the molecules.

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