Quantum Chemical Studies of Diamond for Energy Related Applications

YANG SONG
Abstract


Diamond is a unique material with excellent properties. As a result of the development within the area of CVD synthesis, doping and surface functionalization, diamond has become a strong candidate for use in electrochemical, electronic and biomedical applications. In this thesis, theoretical calculations have been used with the purpose to investigate various properties of the diamond surfaces.

The effect of doping elements (N and B) on the stability of different surface terminations with X (where X = H, OH, O\textsubscript{ontop} or O\textsubscript{bridge}) has been investigated for a diamond (100) surface. As a result, the adsorption energy for all termination types was shown to decrease from the situation with a non-doped diamond surface, to the scenario with a N- (or B-doped) diamond thin film. This result was found to correlate well with the changes of the calculated C\textsubscript{surface}-X bond lengths. Furthermore, the spin density has been calculated and used to show the local distribution of the unpaired electron, which is the consequence of the introduction of dopants into the diamond slab. As a result, the spin density was found to be localized in the vicinity to the dopants for H- (or OH-) terminated diamond (100) surfaces. On the other hand, a delocalised spin density over the O\textsubscript{adsorbate} and C\textsubscript{surface} layer for O\textsubscript{ontop} and O\textsubscript{bridge}-terminated surfaces, has also been observed. Moreover, the results of the pDOS calculations indicate the electron donating ability of N, and the hole donating ability of B. The Fermi level was shifted towards the lower conduction band edge for N-doped diamond, and towards the upper edge of the valence band edge for B-doped diamond. Hence, N-doped diamond will render n-type conductivity, and B-doped diamond will show p-type conductivity. In addition, an interesting observation was made for O\textsubscript{ontop} -terminated diamond surfaces. Localized electron conductivity, involving only this type of termination situation, was also observed for N- (or B-) doped and completely O\textsubscript{ontop}-terminated diamond surfaces.

With the purpose of applying diamond substrates in the formation of epitaxial graphene, the annealing process of an ideal diamond (111) surface has also been simulated in the present work. It was thereby shown that high temperatures (over 2000 K) will be required for the epitaxial formation of graphene ontop of the diamond (111) surface. However, in the presence of hydrogen radicals (by saturating the radical sites in the system), the required temperature was observed to decrease to 1000 K. In addition to these MD simulations, by using an interlayer iron ontop of the diamond (111) surface, the adhesion energies between the graphene and the Fe//diamond slab, as well as the adhesion energy between the graphene//Fe layer and the diamond (111) surface, have been calculated. Thereby, the interaction between the graphene and Fe layer was obtained to be very weak, and of an electrostatic type. On the other hand, the interaction between the Fe interlayer and the diamond substrate was calculated as a moderately strong covalent bond. Moreover, the changes in these interactions, correlating to the changes in the pDOS spectra of graphene, Fe and diamond, gave a tendency of one-dimensional quantum size effect, depending on the thickness of Fe interlayer.

Keywords: Diamond, surface, graphene, terminations, doping, functionalization

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urn:nbn:se:uu:diva-245224 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-245224)
To my wife, kids and parents
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


IV Song, Y., Larsson, K. Theoretical Study of the Effect of an Fe Interlayer on the Formation of Graphene on Diamond (111) Surface. Submitted

Reprints were made with permission from the respective publishers.
My contributions

Paper I  I contributed to the design of work, performed all calculation work and the writing of the manuscript.

Paper II I contributed to the design of work, performed all calculation work and the writing of the manuscript.

Paper III I contributed to the design of work, performed all calculation work and the writing of the manuscript.

Paper IV I contributed to the design of work, performed all calculation work and the writing of the manuscript.
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Abbreviations

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<th>Description</th>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular Dynamic method</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>LDA</td>
<td>Localized Density Approximation</td>
</tr>
<tr>
<td>HTHP</td>
<td>High Temperature High Pressure</td>
</tr>
<tr>
<td>NVT</td>
<td>Canonical Ensemble</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye Sensitized Solar Cell</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of States</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>NCD</td>
<td>Nano Crystalline Diamond</td>
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</table>
1. Introduction

1.1 Diamond
Ever since diamond was found in nature, it became a symbol for hardness, brilliance and eternity. These fortunes that became recognized and loved by mankind, are reflections of its unique physical and chemical properties. After hundreds of years, diamond is still keeping the record of being the hardest known material, having the highest refractive index of any natural mineral, and being well known for its great chemical inertness. It has also many other extraordinary properties.

Diamond is a metastable carbon material that occurs in nature in small quantities. Compared to the most stable carbon material, graphite, diamond is known to have a 0.02 eV/atom higher energy at ambient temperature and pressures. However, the energy barrier between these two carbon phases has been reported as 0.4 eV/atom\(^1\). Therefore, the transition between these two phases is extremely difficult to accomplish. However, the transition was found to take place under high temperature high pressure conditions for the graphite-to-diamond phase transformation, and at a high temperature (over 2000K) for the reverse transformation. On the other hand, the diamond (111) surface has been found to have a very low lattice mismatch relative graphene (of about 2\%).

Recently, by following the explosive interest for graphene, the possibility to form graphene epitaxially onto diamond (111), has been investigated. It has been shown possible to grow graphene at a large area, and with a high quality\(^2\). Structurally, diamond has a face centered cubic (fcc) crystal structure, in which each carbon atom form four strong sp\(^3\)-hybridized C-C bonds. This structural arrangement, in addition to the strong bonds, explains the extreme hardness and high density. Despite the extreme hardness, also the electronic properties of diamond have been found to be unique amongst the carbon allotropes. The band gap of diamond is about 5.45 eV, and it is thereby considered as a wide bandgap semiconductor, or insulator. Due to the occupation of all electrons within the sp\(^3\)-hybridized bonds, there is no charge carrier in non-doped diamond, therefore a very low current is allowed even under high voltage. Moreover, the mobility of charge carriers (electrons and holes) is one of the highest among the wide-band-gap materials. It is significant that for a CVD synthesized single crystalline diamond, an electron mobility of 4500 cm\(^2\)/Vs and a hole mobility of 3800 cm\(^2\)/Vs, have
been reported. Apart from these extraordinary properties, an excellent thermal conductivity, chemical inertness, and bio-compatibility can be attributed to this unique material.

1.2 Synthesis of diamond

During the 19th century, many attempts were made to synthesize diamond by scientists. The first commercially recognized synthetic diamond was produced using a high-temperature high-pressure method (HTHP). With a temperature in the range 1700-2000K and with high pressure (70-80kPa), diamond was synthesized in an environment similar to the earth core. This method has been well developed and is still, nowadays, widely used for the synthesis of diamond for industrial applications. In addition, chemical vapor deposition (CVD) is a very successful method for artificial diamond synthesis, and has become a very versatile method developed during the 90s. As compared with the HTHP method, CVD is a metastable synthesis method by which it is possible to produce diamond at low pressures (600-14000Pa), and at a relatively low temperature (800-1100K). In this process, a gaseous hydrocarbon precursor is introduced into the growth chamber, and mixed with a super saturation of hydrogen. This mixture of gases is then activated by various means. The two most common methods are to use a hot filament or plasma, thereby forming various types of fragments from both the hydrocarbon source, as well as from H₂. By a careful control of the parameter setup, the CVD method can be used to produce various types of diamond. For example, by adding specific precursors to the hydrocarbon/hydrogen mixture, dopant elements such as B, P, N can be introduced into the diamond lattice and thereby bring extra properties to the diamond film. For instance, it has been reported, both experimentally and theoretically, that the growth rate will be affected by the presence of dopants in the diamond lattice. Moreover, the diamond surface texture can be controlled with respect to the designed growth procedure. The most important effect by introducing either B, or N, dopants into the lattice is, though, to give diamond semiconducting properties.

1.3 Doping of diamond

Doping is a process that introduces impurities into an intrinsic semiconductor, and thereby modifies its electronic property. One of the most famous applications for doped diamond is to function as a p-n junction semiconductor in electronic devices. As described above, by using the CVD method, a certain doping element at a specific concentration can in a
highly well-controlled way be added into the diamond lattice during the growth process\textsuperscript{15}. Currently, the most common doping elements are B and N for p- and n-type doping, respectively\textsuperscript{16, 18-19}. Electronic states of the B and N dopants are energetically positioned within the band gap of intrinsic diamond. As can be seen in Figure 1.1, the initially empty state by B is positioned 0.4eV above the upper valence band edge of diamond. For the situation with an N dopant, the initially filled state is position 1.4 eV above the upper valence band edge or 1.7eV below the lower conduction band edge of diamond\textsuperscript{20}.

In summary, the p-type doping (created by B) will thereby induce holes in the valence band of diamond, while n-type doping (created by N) will induce the possibility for electrons in the conduction band of diamond. These charge carriers will render semiconducting properties to diamond, with the other excellent properties maintained.

\textbf{Figure 1.1.} Energy-band diagram for differently doped (using either B or N) diamond.

\subsection*{1.4 Diamond surfaces}

The surface property of a material is as important as its bulk property. Since there are often dangling bonds and defects in the surface area of the materials, it is sometimes difficult to characterize surface properties compared to bulk. Moreover, recombination and reconstruction are two of the most common surface reactions. As a result of these reactions, the surface energy decreases, and the surface will thereby become stabilized. The most common CVD diamond surface planes are (111), (100) and (110) (Figure 1.2). Moreover, these surfaces experiences different properties. For example, the hardness of different diamond surfaces can differ from 6000 to
10000 kgmm$^{-2}$\textsuperscript{21-22}. Hence, in cutting tools applications, diamond coatings with a (111) texture are generally preferred. Energetically, the order of surface energy is (110) (4.1 eV) $>$ (100) (3.8 eV) $>$ (111) (2.7 eV)$^{23}$. However, the (100) surface becomes 2x1-reconstructed (without any accompanying energy barrier), and will thereby lower the surface energy to 2.2 eV (see Table 1.1).

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Absolute Surface Energy (eV/1×1 cell)</th>
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<tbody>
<tr>
<td>(100)</td>
<td>3.8</td>
</tr>
<tr>
<td>(100) (2x1)</td>
<td>2.2</td>
</tr>
<tr>
<td>(110)</td>
<td>4.1</td>
</tr>
<tr>
<td>(111)</td>
<td>2.7</td>
</tr>
<tr>
<td>(111) (2x1)</td>
<td>1.4</td>
</tr>
</tbody>
</table>

It was shown in Paper II, that the surface geometrical structure of diamond (111) will have a lattice mismatch of as low as about 2% when compared with the basal plane of graphite. This can be explained by the fact that the diamond (111) surface is constituted by two surface carbon layers that are very close to each other. This kind of bi-layer surface has the highest density of carbon atoms amongst the low index diamond surface planes.

Apart from the diamond surface structure, surface termination is also a very important factor that will largely influence the surface properties. Hydrogen, H, is the most common terminating species. In fact, CVD syntheses of diamond will most commonly result in an H-terminated diamond film, since there is a super-saturation of hydrogen in the CVD chamber. Moreover, the H-termination makes the diamond surface hydrophobic. This is in contrast to O-termination, which will render a hydrophilic diamond surface. In addition, hydrogen termination has also been found to give a surface electronic conductivity\textsuperscript{24}. In Paper I, the effect by surface termination, as well as the effect of dopants, on surface stabilization, will be discussed in great detail.
1.5 Applications of diamond and outlook

Before the possibility to grow diamond films using vapor phase deposition methods, high-pressure high temperature growth of diamond was mostly used for applications like, e.g., cutting tools. However, with the possibility to synthesize diamond thin films by using CVD methods, several different types of diamond crystallinity can be formed, such as nanocrystalline, microcrystalline, and single crystalline diamond. Due to the electronic properties, thin films of CVD diamond have become of a large scientific interest. With a high break down voltage, extremely high carrier mobility, high thermal conductivity and chemical inertness, doped diamond films will be a strong candidate for applications such as field effect transistor, applications based on electrochemistry at electrodes, sensing, etc.

For the H-terminated diamond surface, since the lower edge of the conduction band is attributed to an energy that is larger than for the vacuum level, diamond is also considered as a material for electron emitters.
Furthermore, excellent biocompatibility makes diamond a new material for drug delivery and bone implantation\textsuperscript{39-41}.

In this thesis, two specific applications of diamond will be presented and discussed. In \textbf{paper III}, B-doped diamond is designed as an electrode material for p-type dye sensitized solar cell applications\textsuperscript{42}. Five different dye molecules (C\textsubscript{20}H\textsubscript{13}NO\textsubscript{3}S\textsubscript{4}, C\textsubscript{35}H\textsubscript{37}NO\textsubscript{2}S\textsubscript{3}, C\textsubscript{34}H\textsubscript{38}OS\textsubscript{2}, C\textsubscript{32}H\textsubscript{36}OS\textsubscript{2} and C\textsubscript{31}H\textsubscript{35}S\textsubscript{3}Br) will be thereby be chemisorbed to an H-terminated diamond (111) surface. The aim with the study in \textbf{paper III} is to achieve a fundamental understanding of how the dopant (B) can affect the electronic structure of these systems. In addition, diamond has been investigated as the substrate for large area epitaxial graphene growth on the diamond (111) surface (\textbf{Paper II and IV})\textsuperscript{43-46}.

\section*{1.6 Aim of thesis}

The main objectives of the work presented in this thesis, have been to understand and further develop the possibility for applying diamond material in various applications. The first part of the work is focusing on the effect of dopants (N and B) on diamond surface properties. The work describing the effect of B on the adsorption of various dye molecules for solar cell applications will be included in this first section. The second part of the work, presents the diamond-to-graphene formation. More specifically, the effect by the introduction of H radicals in the diamond (111) surface region, or by using a thin Fe film onto diamond (111) surface, has been carefully investigated. Generally, DFT calculations have, with one exception, been used in the present Thesis. The effect by the introduction of H radicals in the diamond surface region was modeled by using \textit{ab initio} dynamics simulations at realistic temperatures.
2. Theoretical methods and models

2.1 General
By following the development of computational techniques, the efficiency and accuracy of theoretical calculations have increased dramatically the last decades. Density Functional Theory (DFT)\(^{47-48}\), as an *ab initio* method, is one of the most widely used theoretical approaches at the moment. In the DFT calculations, the simulated materials are described with an electron density distribution. The *ab initio* Molecular Dynamic calculation (MD)\(^{49}\) is a method that usually describes the structural dynamics on the atomic/molecular scale, and at more realistic temperatures.

2.2 Density Functional Theory
The Schrödinger equation, which is the fundamental equation within quantum mechanics, is described in full as the time-dependent, many-body equation (see eq. 2.1):

\[
\frac{i\hbar}{\partial t} \Psi = H \Psi
\]  

(2.1)

For most of the calculations in the present thesis, a simplified version of the Schrödinger equation has been used, based on stationary states of systems with fixed positions of atoms (see eq. 2.2),

\[
H \Psi = E \Psi
\]

(2.2)

A Hamiltonian operator, \(H\), acting on a wave function, \(\Psi\), is used to obtain the total energy, \(E\), of the system. Within this equation, the Hamiltonian is composed by the kinetic energies of the electrons, the Coulomb potential for electron-nucleus interactions, and electron-electron and nucleus-nucleus repulsive interactions. Moreover, for many electronic systems, equation 2.2 must be even more simplified in order to be solved. Therefore, the Born-Oppenheimer approximation has been used, which is based on the observation that electrons are much lighter and faster than the nuclei. As a
consequence, the atomic nuclei have been treated as fixed in relation to the electrons.

To further simplify the Schrödinger equation, the Hartree-Fock method was introduced in order to treat the particles of the investigated system as independent from each other. Within this approximation, the total wave function for an N electron system has been described with a Slater determinant including terms that are based on independent single electron wave functions. As another important approach for describing the ground state electronic structure systems, the Density Functional Theory (DFT) transforms the wave functions of the electrons to electron densities, $\rho$, (see eq. 2.3):

$$\rho = \sum_{i}^{N} |\Psi_i|^2$$  \hspace{1cm} (2.3)

Accordingly, the total energy of the system is expressed as:

$$E[\rho] = T[\rho] + J[\rho] + E_{XC}[\rho] + V_{Ne}[\rho]$$  \hspace{1cm} (2.4)

where $E[\rho]$ is the total energy, $T[\rho]$ is the term of kinetic energy of a non-interacting system, $J[\rho]$ is the electron-electron coulomb interaction, $V_{Ne}$ is the electron-nucleus interaction, and $E_{XC}$ is the exchange-correlation energy. In this equation, the unknown term $E_{xc}$ is the exchange-correlation functional for the electron-electron interactions. Hence, approximations must be introduced to try to express the instantaneous electron-electron correlations. The Local Density Approximation (LDA) is the simplest approach to describe this correlation-exchange term (see eq. 2.5). It is a commonly used approximation for most of the homogenous gases and simple metal. However, the LDA approximation has been found to overestimate the bond strength in covalent materials (e.g., in semiconductors). However, the Generalized Gradient Approximation (GGA) is a better approximation that involves the gradient of the charge density, $\nabla \rho$, in order to describe the non-homogeneity of the electron density for these latter types of materials (see eq. 2.6).

$$E_{XC}^{LDA} [\rho] = \int \rho(\vec{r}) \epsilon_{XC} (\rho) d\vec{r}$$  \hspace{1cm} (2.5)

$$E_{XC}^{GGA} [\rho] = \int \rho(\vec{r}) \epsilon_{XC} (\rho, \nabla \rho) d\vec{r}$$  \hspace{1cm} (2.6)

Many functionals (such as PW91, PBE and BLYP) have been developed to describe covalent materials\textsuperscript{50-53}. Also, hybrid functionals (e.g. B3LYP and PBE0)\textsuperscript{54-55}, including a partial Hartree-Fock exchange, have been developed.
However, during the development of DFT functional, more complex interactions including long-range dispersion, and strong electron Columbic interactions within the d/f orbital, have been found difficult to handle in the exchange-correlation functionals. Therefore, empirical corrections (e.g., TS corrections and Hubberd U) are often used for specific systems\textsuperscript{56-58}. 

2.3 Molecular Dynamics

Molecular Dynamics (MD) is a well known computational method with which it is possible to simulate dynamic processes on the atomic scale. Unlike the description of a stationary system, time and temperature are important parameters that are involved in the MD calculations. Furthermore, the effect of pressure and other dynamical parameters are possible to be considered when using this method. The atoms in the constructed models are allowed to interact with each other via forces that are defined as inter-atomic potentials. The potentials used in the MD calculations are usually classified as empirical or \textit{ab initio} potentials. The empirical potentials are also called force fields, and they contain various system-related information, such as chemical bonds, dispersions and bond angles. On the other hand, \textit{ab initio} MD (AIMD) is a relatively computational expensive method, and is usually used for smaller systems and shorter simulation times\textsuperscript{59-60}. However, properties such as electronic structure, density of states and formation/deformation of covalent bonds, can be simulated more accurately.

Ensembles are designed constraints within molecular dynamics simulations. For instance, an NVT ensemble, which was used in \textit{paper II}, regulates the system with fixed number of particles (N), volume (V) and temperature (T). With this setup, the system is allowed to have an energy-activated structural evolution in a constant thermal bath\textsuperscript{61}.

2.4 Models and parameters setup

The investigations presented in the present Thesis do all consider surface chemistry on diamond surfaces. Therefore, in order to be able to observe the properties of the material, such as surface geometrical changes, or to simulate a reasonable doping concentration, larger super-cells of diamond surfaces have been used; 4x4x6 (\textit{Paper I}), 6x6x12 (\textit{paper II}), and 7x7x6 (\textit{papers III} and \textit{IV}) have been used. The CASTEP program has been used for these calculations. To simulate the surfaces, the models were made infinite under periodic boundary conditions in the x- and y- directions. In addition, a vacuum slab with a proper thickness was used in the z-direction. Any interactions between the supercell layers were thereby eliminated. Furthermore, in the bottom layer of each surface model, the carbon atoms
were saturated with H and constrained during the geometry optimization calculations. A continuation of the system towards a bulk situation was thereby simulated. An exception is the dye molecules (Paper III) which were modeled as single molecules (as shown in Figure 2.1). The Dmol3 program was used for these calculations.

Figure 2.1. Dye molecules, as presented in Paper III: A) C_{20}H_{13}NO_3S_4, B) C_{35}H_{37}NO_2S_3, C) C_{34}H_{38}OS_2, D) C_{32}H_{36}OS_2, and E) C_{31}H_{35}S_3Br.

For the DFT calculations performed using the CASTEP module, a plane wave basis was used in a way to describe delocalized and extended molecular orbitals. At this point, the choice of a finite number of plan waves is critical for (1) maintaining the accuracy in describing large and complicated system, and (2) minimizing computational time. Hence, the energy convergence for specific cut-off energy, in combination with k-points, has been carefully tested for each model. To simulate the core level of the atoms in the materials, two methods have been used; ultra-soft pseudopotential approximations (when using CASTEP), and an all electrons basis set (when using Dmol3). The all electron basis sets were used in order to identify the energy levels of the dye sensitizer’s frontier orbital in relation to the vacuum level. On the other hand, to overcome the expensive core level calculations, an ultra-soft pseudopotential were used for the larger surface models.

For the investigations involving unpaired electrons in the model (e.g., for the doped diamond surfaces), spin polarized methods were used. In those calculations, the alpha and beta spins were described by using different wave
functions. With this set up, the sum of these two charge densities results in the total charge density, and the difference gives the spin density of the system. In addition, the result from spin-unrestricted calculations can be visualized in order to identify the model sites that contain partial spin density (as discussed in Paper II).

2.5 Energy calculations

In Paper IV, adhesion energies have been used to describe the interfacial binding conditions between the adlayer and the diamond surface. It usually contains strong interactions such as covalent bonds, and weak interactions such as electrostatic interactions and Van der Waals forces. As discussed in Section 2.2, the Van der Waals interactions are generally not accounted for in most of the DFT functionals of today. Within the present Thesis, weak interaction corrections have been applied to consider also these types of energy interactions;

\[ E_{adh} = E_{tot} - E_A - E_B \]  \hspace{1cm} (2.7)

where \( E_{tot} \) is the total energy of the system (containing both layers), and \( E_A \) and \( E_B \) is the energy of layer A and B, respectively. The latter energies were calculated with the same supercell size, in addition to the same parameters, as was used for the total models.

The average adsorption energies, \( \Delta E_{ads} \), have been used to quantify the chemisorption of the individual adsorbates onto the diamond surface.

\[ \Delta E_{ads,avg} = \frac{1}{n} \left[ E_{surface-X} - E_{clean} - E_X \right] \]  \hspace{1cm} (2.8)

where \( E_{surface-X} \) is the total energy for the chemisorbed surface, \( E_{clean} \) is the energy for a non-terminated surface, and \( E_X \) is the total energy for the adsorbates.

In paper I, in concomitant with the adsorption energy, the relative stabilization energy with respect to hydrogen termination has been calculated as:

\[ E_{stab, (XrelativeH),avg} = E_{ads,X} - E_{ads,H} \]  \hspace{1cm} (2.9)

where \( E_{ads,X} \) and \( E_{ads,H} \) are the adsorption energies for the adsorbate X (OH-, O_{ontop}- and O_{bridge}-terminations) and H, respectively (Paper I).
2.6 Property analysis methods

Density of states (DOS) is an effective mathematical tool for electronic structure analysis. By using equation 2.10, the DOS for an electron band n, $N_n(E)$, has been calculated as the integral over the Brillouin zone. The output of the DOS analysis in the present thesis is based on a linear interpolation of the parallelepiped formed by using the k-points from the Monkhorst-Pack set. It is further treated by the histogram sampling of the band energy results.

$$N_n(E) = \int \frac{dk}{4\pi^2} \delta(E - E_n(k)) \quad (2.10)$$

The assignment of atomic charges and electronic bond populations for the specific atoms and bonds in the model systems, are widely used analysis methods in understanding the electronic structures of the systems. For the DFT calculations in the present Thesis, the population analysis has been performed by using the Mulliken formalism. However, due to the delocalized nature of a plan wave basis set, the plane wave-related electron densities have been projected onto the localized basis sets. In Paper I, the comparison of Mulliken atomic charges and electron bond populations of specific atoms and bonds, have been compared for different doping conditions in studying the chemisorption of X to the diamond surface (X = H-, OH-, Oontop- and Obridge- terminating species, respectively). In Paper III and IV, a bond population analysis has been made in order to analyze the partial charge transfer between the diamond surface and the adsorbates (or adlayers).

Fukui Functions (Eq. 2.11), developed by Fukui et. al in 1952, are reliable indicators for surface reactivity analysis. By looking into frontier orbital, and by either add, or remove, electrons to the systems, the susceptibility to an electrophilic ($f^-$, Eq. 2.12), nucleophilic ($f^+$, Eq. 2.13), or radical ($f^0$, Eq. 2.14) attack, can be calculated for the systems under investigation.

$$f(r) = \left( \frac{\partial \rho(r)}{\partial N} \right) V(r) \quad (2.11)$$

$$f^+ = \frac{1}{\Delta N} \left( \rho_{N+\Delta}(r) - \rho_N(r) \right) \quad (2.12)$$

$$f^- = \frac{1}{\Delta N} \left( \rho_N(r) - \rho_{N-\Delta}(r) \right) \quad (2.13)$$
\[ f^0 = \frac{1}{2} \left( \rho_{N+\Delta}(r) - \rho_{N-\Delta}(r) \right) \] (2.14)

In summary, these Fukui functions can be mapped onto an electron density surface with the purpose to indicate surface reactivity towards different kinds of chemical reactions (i.e., adsorption) with the environment.
3. Surface properties of diamond with respect to different surface terminations and dopants

3.1 Introduction

Surfaces can be defined as a two-dimensional topological space in mathematics, one kind of tablet computers in electronics, or what will be discussed in this chapter - the boundary of a three dimensional material within surface science.

In the surface area of a material, due to the restrictions of binding atomic neighbors, the reactivity is usually higher than in the bulk. In nature, this usually leads to adsorption of reactive gases to the surface, or reactions between surface atoms and aquatic ions. The surface region will thereby be somewhat stabilized. In the development of surface science during last decades, the community has gained enough knowledge to modify the surfaces in such a way that specific elements, or functional groups, can be attached to the surfaces for the need of various applications (i.e., growth, sensing, and electron transport).

Doping of the diamond material is most often processed as a substitutional replacement of C atoms with dopant atoms. By doping, the properties of the dopant (such as electronic states and electronegativity), will be blended with the corresponding properties of the hosting material. By doping diamond with certain elements, and with certain concentrations thereof, the possibility for extraordinary applications have been reported; superconductivity of B-doped diamond, applications of N-doped diamond in microelectronics, increased growth rate of CVD diamond	extsuperscript{ed}, etc.

In this chapter, the effect of substitutional dopants on the diamond surface stabilization, for several types of surface termination species, will be especially discussed. According to previous investigations concerning the effect on surface stabilization by surface coverage (of specific surface terminating species), the coverage of all investigated termination types has in this thesis been set to 100%. By performing accurate DFT calculations, in addition to analysis of the electronic, geometrical and energetic properties of the different terminated diamond surfaces, the role of both typical n- and p-type dopants (N and B, respectively), has here been investigated.
3.2 Surface geometrical structures

With the dopants positioned in the second atomic C layer of the 2x1 reconstructed diamond (100) surface, the binding conditions for the surface terminating species close to the dopants were found to differ appreciably from the non-doping scenario. As can be seen in Table 1, the bond lengths of these species changed markedly with respect to termination and dopant types.

For the H-terminated diamond surface, the dopants were found to affect the length of the C-H bonds with an increase in bond length of 0.009 Å (N-doping situation) and 0.006 Å (B-doping situation). However, for the OH-, O_{ontop}- and O_{bridge}-termination types, the lengths of the C-O bonds decreased for the N-doped situation, approximately 0.04, 0.02 and 0.08 Å for OH-, O_{ontop}- and O_{bridge}-termination, respectively. For the situation with B-doping, these bonds did in fact increase; approximately 0.02, 0.01 and 0.03 Å for OH-, O_{ontop}- and O_{bridge}-termination, respectively. An analysis of these results will be presented and discussed in Section 3.4 Electronic population analysis.

Table 3.1. Surface – terminator (X) bond lengths for X adsorbates close to the dopant N (or B) (X = H, OH, O_{ontop}, and O_{bridge}). It has to be noticed that there are two C-X bonds for H-, OH-, O_{ontop}-terminations, in addition to four C-O_{bridge} bonds.

<table>
<thead>
<tr>
<th>Terminations</th>
<th>Bond length (Å) (N-doped)</th>
<th>Bond length (Å) (B-doped)</th>
<th>Bond length (Å) (non-doped)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.109, 1.109</td>
<td>1.107, 1.106</td>
<td>1.100, 1.100</td>
</tr>
<tr>
<td>OH</td>
<td>1.366, 1.374</td>
<td>1.432, 1.425</td>
<td>1.408, 1.409</td>
</tr>
<tr>
<td>O_{ontop}</td>
<td>1.192, 1.192</td>
<td>1.216, 1.216</td>
<td>1.207, 1.207</td>
</tr>
<tr>
<td>O_{bridge}</td>
<td>1.411, 1.413, 1.535, 1.537, 1.504, 1.504</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In addition to these results regarding changes in bond lengths, bond distortions were also observed for both types of doped diamond surfaces. As an example of distortions, the results for O_{ontop}-terminated diamond surfaces are presented in Fig.3.1. In this figure, the changes in the angle X (terminator)-C (layer 1)-C (layer 2) can be observed. It is obvious that for the N-doped scenario, the O_{ontop} -terminating species will pairwise move towards each other. On the contrary, these O_{ontop} -terminating species moved away from each other in the case of a B-doped surface. The covalent radii of C, N and B atoms are different with respect to each other; 0.76, 0.71 and 0.84 Å, respectively. Hence, the displacement of the surface adsorbates, O atoms in this case, will also differ. This observation is most probably due to the different degree of surface relaxation and reconstruction processes, which in turn are caused by the size of the substitutional dopants.
3.3 Energetic comparisons

In comparison with a non-doped (i.e., intrinsic) diamond (100) surface, the effect of doping on the adsorption energy for terminating species attached to a diamond (100) surface, will be discussed in the present Section. In addition, the stabilization energies relative the H-termination scenario, will also be presented for all termination types. As shown in Fig. 3.2, the order of adsorption energies for the doped and non-doped diamond systems is: \( E_{\text{ads}} \) (B-doped) > \( E_{\text{ads}} \) (N-doped) > \( E_{\text{ads}} \) (non-doped). The adsorption energy for the non-doped surface is, hence, most negative, and this type of surface is therefore most reactive. Moreover, the negative adsorption energy values show that these adsorption reactions are exothermic. Furthermore, as a comparison among the termination types, the result of the relative stabilization energies provided the order of stabilization energies as \( \text{O}_{\text{bridge}} < \text{O}_{\text{ontop}} < \text{H} \) (reference point) < OH-termination. Also here, the most negative stabilization energy (as for \( \text{O}_{\text{bridge}} \)-termination) corresponds to the most stable situation. In general, the order of stabilization energies indicates the ability of stabilizing the surface carbon atoms by different termination species.

3.4 Electronic population analysis

3.4.1 Atomic charges and electron bond population analysis

With a strong correlation to the geometrical changes discussed in Section 3.1, the atomic charges of the dopant B (or N) with its surrounding atoms, are shown in Table 3.2. In addition to the results presented in Table 3.2, the corresponding bond population values are presented in Table 3.3.
Figure 3.2. Calculated adsorption energies ($E_{\text{ads}}$), in addition to H-related stabilization energies ($E_{\text{sta}}$), for variously X-terminated (X = H, O$_{\text{ontop}}$, OH, and O$_{\text{bridge}}$), and doped (non-, N-, and B-doped) diamond (100) surfaces.

Figure 3.3. Surface geometrical structures for the region surrounding the N (or B) dopant. The labelling of the individual atoms corresponds to Table 3.2 and 3.3, respectively.
Table 3.2. *Atomic charges (Mulliken) of the N (or B) dopants, and its surrounding atoms, for various termination types (H, OH, O$_{ontop}$ and O$_{bridge}$).*

<table>
<thead>
<tr>
<th>Termination type</th>
<th>Atoms</th>
<th>Non-doped</th>
<th>N-doped</th>
<th>B-doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H1</td>
<td>0.24</td>
<td>0.28</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>H2</td>
<td>0.24</td>
<td>0.28</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>-0.25</td>
<td>-0.15</td>
<td>-0.40</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>-0.25</td>
<td>-0.15</td>
<td>-0.40</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>-0.01</td>
<td>0.12</td>
<td>-0.12</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>0.02</td>
<td>0.10</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>C/N/B</td>
<td>0.01</td>
<td>-0.15</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(H)1</td>
<td>-0.70</td>
<td>-0.67</td>
<td>-0.71</td>
<td></td>
</tr>
<tr>
<td>O(H)2</td>
<td>-0.70</td>
<td>-0.66</td>
<td>-0.71</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>0.20</td>
<td>0.31</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>0.20</td>
<td>0.31</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>-0.01</td>
<td>0.12</td>
<td>-0.12</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>0.02</td>
<td>0.10</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>C/N/B</td>
<td>-0.02</td>
<td>-0.18</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>O$_{ontop}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>-0.33</td>
<td>-0.30</td>
<td>-0.34</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>-0.33</td>
<td>-0.30</td>
<td>-0.34</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>0.39</td>
<td>0.45</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>0.39</td>
<td>0.45</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0.01</td>
<td>0.12</td>
<td>-0.13</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>0.01</td>
<td>0.12</td>
<td>-0.13</td>
<td></td>
</tr>
<tr>
<td>C/N/B</td>
<td>-0.09</td>
<td>-0.23</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>O$_{bridge}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O1</td>
<td>-0.43</td>
<td>-0.39</td>
<td>-0.42</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>-0.43</td>
<td>-0.40</td>
<td>-0.42</td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>-0.43</td>
<td>-0.41</td>
<td>-0.42</td>
<td></td>
</tr>
<tr>
<td>O4</td>
<td>-0.43</td>
<td>-0.41</td>
<td>-0.42</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>0.44</td>
<td>0.57</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>0.44</td>
<td>0.56</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>-0.01</td>
<td>0.10</td>
<td>-0.15</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>-0.01</td>
<td>0.10</td>
<td>-0.15</td>
<td></td>
</tr>
<tr>
<td>C/N/B</td>
<td>-0.02</td>
<td>-0.20</td>
<td>0.33</td>
<td></td>
</tr>
</tbody>
</table>

The N element is the most electronegative one when compared with B and C. It is here shown that N have a negative atomic charge for all diamond systems investigated. As a consequence, the surrounding carbon atoms are shown to have a less negative atomic charge; -0.25(non-doped) vs. -0.15(N-doped). For the situation with OH-termination, the surrounding carbon atoms will be more positively charged; +0.20(non-doped) vs. +0.31(N-doped). Moreover, the charges of the closest H-terminating atoms, which link to the N-connecting surface carbon atoms, are slightly increased. On the other hand, the charges of the O-terminating atoms are shown to decrease for the N-doped diamond systems (see Table 3.2.). As was the situation with N doping, the B dopant, with its lower value of electronegativity besides H, are shown to have a positive atomic charge for all systems investigated. As a consequence, the atomic charges of its...
surrounding atoms have here been shown to have numerical values that are opposite to the ones achieved for the N-doped systems. For the H-terminating situation, the surface C atomic charge will go from -0.15 for the non-doped situation, to -0.40 for the B-doped situation. For OH-termination, the corresponding values are +0.2 (non-doped) vs. +0.6 (B-doped). These observations are strongly correlating to the electron density withdrawn ability by N, and the donating ability by B. The underlying reason is the difference in electronegativity; B (2.04), C (2.55) and N (3.04), respectively\textsuperscript{65}.

Table 3.3. The electron bond population values for various bonds in the vicinity of the N (or B) dopant. For comparison, the corresponding values for non-doped diamond are also shown. The terminating species are H, OH, O\textsubscript{ontop} and O\textsubscript{bridge}, respectively. The labelling of the atoms refers to Fig. 3.3.

<table>
<thead>
<tr>
<th>Termination type</th>
<th>Bonds</th>
<th>Intrinsic</th>
<th>N-doped</th>
<th>B-doped</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H1-C1</td>
<td>0.88</td>
<td>0.80</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>H2-C2</td>
<td>0.88</td>
<td>0.80</td>
<td>0.86</td>
</tr>
<tr>
<td>C1-C/N/B</td>
<td>0.82</td>
<td>0.61</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>C2-C/N/B</td>
<td>0.82</td>
<td>0.62</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>C3-C/N/B</td>
<td>0.8</td>
<td>0.62</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>C4-C/N/B</td>
<td>0.81</td>
<td>0.59</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>O(H)1-C1</td>
<td>0.59</td>
<td>0.64</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>O(H)2-C2</td>
<td>0.59</td>
<td>0.66</td>
<td>0.56</td>
</tr>
<tr>
<td>C1-C/N/B</td>
<td>0.82</td>
<td>0.60</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>C2-C/N/B</td>
<td>0.81</td>
<td>0.58</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>C3-C/N/B</td>
<td>0.79</td>
<td>0.64</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>C4-C/N/B</td>
<td>0.81</td>
<td>0.59</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>O\textsubscript{ontop}</td>
<td>O1=C1</td>
<td>1.22</td>
<td>1.26</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>O2=C2</td>
<td>1.22</td>
<td>1.26</td>
<td>1.17</td>
</tr>
<tr>
<td>C1-C/N/B</td>
<td>0.79</td>
<td>0.47</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>C2-C/N/B</td>
<td>0.79</td>
<td>0.47</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>C3-C/N/B</td>
<td>0.78</td>
<td>0.64</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>C4-C/N/B</td>
<td>0.78</td>
<td>0.64</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>O\textsubscript{bridge}</td>
<td>O1-C1</td>
<td>0.56</td>
<td>0.64</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>O2-C1</td>
<td>0.56</td>
<td>0.70</td>
<td>0.52</td>
</tr>
<tr>
<td>O3-C2</td>
<td>0.56</td>
<td>0.64</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>O4-C2</td>
<td>0.56</td>
<td>0.65</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>C1-C/N/B</td>
<td>0.82</td>
<td>0.49</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>C2-C/N/B</td>
<td>0.82</td>
<td>0.54</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>C3-C/N/B</td>
<td>0.79</td>
<td>0.65</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>C4-C/N/B</td>
<td>0.78</td>
<td>0.65</td>
<td>0.80</td>
<td></td>
</tr>
</tbody>
</table>

However, as being different from the electronegativity effects, it must be stressed that the N (or B) dopants, also has the ability to donate (or accept) partial electron density to (or from) the surrounding environment. This is due to the one extra (or less) electron in their valence orbitals. As shown in Table 3.3, for the situation with N doping, the electron bond population within the closest C-H (or C-O) bonds are shown to decrease (or increase) compared to
the non-doped diamond surfaces. It can be concluded that the extra electron within N, will partially fill the anti-bonding states of the C-N and C-H bonds, respectively. Hence, decreased electron bond population will be the results, with resulting longer bond lengths. In contrary to these observations, the binding states of the surface C-O bonds will be enhanced by the existence of the donated electron density from N. Hence, the corresponding electron bond populations will be increased, by a shortened C-O bond length.

As compared with the results for the N-doping situation, opposite results were obtained for the B-doping scenario (see Table 3.3). For an H-terminated diamond surface, it has been shown that the bond populations within the closest C-H bonds (relative to the B element), decreased from 0.88 to 0.86. For the corresponding OH-, and O-termination situations (for O\text{ontop}- and O\text{bridge}-termination), decreased bond population values were observed as well (from 0.59 to 0.58 for OH-termination, 1.22 to 1.17 for O\text{ontop} –termination, and 0.56 to 0.52 for O\text{bridge}-termination) for the closest C-O bonds, were found as well. The reason behind these changes is most probably due to the fact that the B atom has one electron less compared to C. Hence, the electron density within the closest C-H and C-O bonds will be somewhat withdrawn towards the C-B bonds, and thereby decreasing the electron bond populations within the surrounding C-X bonds, while at the same time increasing the bond lengths (X = OH, O\text{ontop} and O\text{bridge}).

3.4.2 Electron spin distribution and pDOS analysis

As discussed above, the nature of N (or B) dopants will induce an unpaired electron (i.e., spin) in the modeled systems. Thus, information about the distribution of this spin is important for the resulting electronic properties of the diamond systems under investigation. The spin density distribution is shown in Fig. 3.4. As for all termination types investigated, the electron spin density for the N- (or B-) doped diamond surfaces, is observed to be distributed in the upper surface carbon layer, or even within the termination layer. However, there are minor differences for the various termination scenarios. For H- and OH-terminated diamond surfaces, the spin densities were observed to be localized in the surrounding of the dopants (see Fig. 3.4b). For the O\text{ontop}– and O\text{bridge}-termination situations, the delocalized spin density distributions were observed to concentrate on either the surface carbon layer or within the O-termination layer. As shown in Figure 3.4c, the spin density was generally found to be distributed over the O\text{ontop} layer. The only exception to this situation involved the O atoms that were positioned in line with N. For all systems investigate in the present thesis, the most reactive surface was observed for a B-doped and O\text{ontop}– terminated diamond surface (see Figure 3.4c*). A delocalized spin density was observed within
the O_{ontop} layer, with an exception of a more concentrated spin density on the O atoms in line with the B dopant. In addition, the carbon atoms in the second surface layer, and in line with B, were also found to have distribution of spin density. For the N-doped and O_{bridge}-terminated surface, the spin density was observed to have a delocalized distribution over the first layer C atoms. More specifically, this was the situation for C atoms within, and next to, the line including N. For the situation with B doping, a delocalized spin density was observed for the O_{bridge} adsobates that are situated closest to the dopant.

Figure 3.4. Spin density distributions for a) H-terminated N-doped, a*) H-terminated B-doped, b) OH-terminated N-doped, b*) OH-terminated B-doped, c) O_{ontop}-terminated N-doped, c*) O_{ontop}-terminated B-doped, d) O_{bridge}-terminated N-doped, and d*) O_{bridge}-terminated B-doped diamond (100) surfaces, respectively.
Figure 3.5. Partial Density of States for a) H-terminated and N-doped, a*) H-terminated and B-doped, b) OH-terminated and N-doped, b*) OH-terminated and B-doped, c) O_{bridge}-terminated and N-doped, c*) O_{bridge}-terminated and B-doped, d) O_{ontop}-terminated and N-doped, and d*) O_{ontop}-terminated and B-doped diamond (100)-2x1 surfaces, respectively.
To further investigate the surface electronic structures for the variously terminated diamond (100) surfaces, partial Density of State (pDOS) analysis have here also been performed.

The results of the pDOS calculations are shown in Fig. 3.5 for all types of surface terminations, and for both the N- and B-doped situations. As expected, the main effects by the dopants are the positions of the Fermi levels. In case of N-doped diamond surfaces, the Fermi levels were observed to be closed to the lower edge of the conduction band (due to the existence of the extra electron donated by N). On the contrary, the pDOS spectra for the B-doped scenarios involved Fermi levels that were shifted to the upper edge of the valence band (because of the lack of one electron from B, as compared with C).

However, there is one exception from this overall picture. That concerns the pDOS spectra for the O_{ontop}-terminated diamond surfaces. As shown in Figs. 3.5c and c*, a partial filled p-DOS around the Fermi level has been observed for both the N- and B-doped diamond (100) surfaces. This surprising result indicates the occurrence of a very strict adsorbate layer electronic conductivity. In previous studies, surface conductivity layers have been observed predominantly for the H-terminated diamond surface. The reason for this behavior is most probably the fact that H will lower the ionization energy, and, hence, allow electrochemical redox reactions to occur on the diamond surface. In addition, O-terminated diamond surfaces were also reported to show electronic conductivity within the surface layer\textsuperscript{66-67}. However, the surface conductivity observed in this investigation was considered as a consequence of C=O double bonds. To verify this observation, the pDOS spectra for only the O_{ontop}-termination layers, are presented in Fig. 3.6. Based on these result, it is obvious that the conductivity appears from the O_{ontop}-termination layer only. Moreover, the electron spin density map, as presented above, will further support this conclusion, It is thereby clear that the conductivity of the terminating O_{ontop}...
layer is closely correlated to the localized spin density distribution within this specific type of adsorbate layer.

3.5 Application of B-doped diamond in p-type dye sensitized solar cells (DSSC)

As discussed in the previous sections, by introducing dopants into the diamond lattice, it is possible to modify the properties of the material. For B-doped diamond, free charge carriers can be obtained from the B-related bond gap state 0.4 eV above the upper edge of the valence band. By combining the natural properties of diamond, such as wide electrochemical window and extraordinary carrier mobility, B-doped diamond becomes an excellent candidate in the applications of electronic devices. In this chapter, B-doped diamond-based DSSC will be modeled and analyzed theoretically. An example of the investigated model is shown in Figure 3.7.

*Figure 3.7. A model of a dye (C_{32}H_{36}O_{2}) being adsorbed on the H-terminated B-doped diamond (111) surface.*
3.4.1 Construction of a B-doped diamond-based dye sensitized solar cell

The scheme of a p-type DSSC can be seen in Fig. 3.8. It is a closed circuit and includes the B-doped diamond substrate with adsorbed dyes, a counter electrode, and a redox couple (that collects holes). When the dye sensitizers absorb sunlight, the electrons in the HOMO of the dye will be excited to its LUMO level. As the upper edge of the valence band of the diamond surface is energetically positioned above the HOMO level of the dye molecules, the holes created during the sunlight harvesting process will be injected into the valence band of the diamond surface. Furthermore, driven by the negative potential difference between the upper edge of the diamond valence band and the redox couple, the holes will be transferred to the counter electrode in the solar cell system. Thereafter, by exchanging electrons with the LUMO of the dye sensitizers, the electricity generation process will form a closed circuit.

However, besides these building blocks in the construction of a dye sensitized solar cell system, there are several factors that will affect, or even dominate, the properly functioning of a DSSC (e.g., charge carriers mobility in the material, electron-hole recombination, energy-band matching between the dye and the diamond surface, etc.). Hence, one of the main factors to consider and analyze more thoroughly, is the adsorption of the dye molecules to the diamond surface.

Figure 3.8. The scheme of a B-doped diamond-based DSSC
3.4.2 pDOS analysis

The model in Fig. 3.7 visualizes the position of B in the diamond surface. More specifically, it has been substitutionally positioned within the third atomic C layer. By changing the substitutional position of B to the second surface C layer, it will be possible to study the effect of B position on the pDOS spectra for the adsorbed dye sensitizer. The result is shown in Fig. 3.9 below. It is quite straightforward that in Fig. 3.9A, B and C, the changes in pDOS spectra close to the Fermi level is more pronounced than the ones shown in Figs. D and E. This indicates that the position of B in the diamond lattice might have a profound effect on the frontier orbital electronic structure of the adsorbed dye molecules.

Figure 3.9, DOS spectra for various dye molecules adsorbed onto the B-doped diamond (111) surfaces. For each of these spectra, the solid lines show the result for the situation with B substitutionally positioned in the second C layer of the diamond surface, and the dotted line represents the result when B is positioned within the third C layer. A to E are the dye molecules presented in Section 2.4.

In Fig. 3.9A, an energetically lower positioned LUMO of the sensitizer can be found when B is in the second C surface layer (0.2 eV); as compared to the situation with B in the third C layer (0.6 eV). The HOMO level was though unchanged. These results lead thereby to a difference in the HOMO-LUMO gap (1.4 vs. 1.8 eV). Hence, this band gap is rather sensitive to the position of B in the lattice. Similar observations of changed HOMO-LUMO gaps, with respect to B in different atomic layers, were made for the situation
with dyes B (1.5 vs. 1.8 eV) and C (1.3 vs. 2.0 eV), respectively. The change in DOS spectra as a function of B position, are, however, minor for the dyes D and E. Only a slightly narrowed HOMO-LUMO gap can be observed for D (0.05 eV) and E (0.2 eV).

3.4.3 Population analysis

The position of B in the diamond lattice was above shown to influence the electronic structure of especially the adsorbed dyes A, B, and C. However, the effect by different B positions on the binding conditions between the adsorbates and the diamond substrate remains unknown. In this section, the effect by B position on the stability of the dye molecules, when chemisorbed to the diamond surface, will be discussed and analyzed.

What is common for all dye molecules within the present study, is that they all have a benzene group by which they are allowed to bind to the diamond surface. The adsorption bond strengths, which will be estimated by calculating the electron bond populations, will thereby reflect the stability of this $C_{\text{diamond}}-C_{\text{dye}}$ bond. The electron bond populations for various dyes adsorbed on different B-doped diamond surfaces, are shown in Table 3.4.

<table>
<thead>
<tr>
<th>Dye Molecules</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-doped diamond (2nd layer)</td>
<td>0.93</td>
<td>0.86</td>
<td>0.90</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>B-doped diamond (3rd layer)</td>
<td>0.84</td>
<td>0.83</td>
<td>0.87</td>
<td>0.88</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Electron bond population values are measures of the degree of covalency in the bonds. Hence, a larger numerical value represents a stronger covalent bond. As can be seen in Table 3.4, the C-C bonds between dye adsorbates and the diamond surface are somewhat stronger when B is positioned within the second C layer. In order to estimate the degree of iconicity in these bonds, partial electron transfers between the diamond substrate and the dye molecules have also been calculated, and are presented in Table 3.5.

<table>
<thead>
<tr>
<th>Dye molecules</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-doped diamond (2nd layer)</td>
<td>0.20</td>
<td>0.09</td>
<td>0.13</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>B-doped diamond (3rd layer)</td>
<td>0.19</td>
<td>0.09</td>
<td>0.12</td>
<td>0.08</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The partial electron transfer from the B-doped diamond surface to the dye adsorbates, has been found to be somewhat more pronounced for the situation with B in the second surface C layer. This is a result that strongly
correlate with the bond population results, and, hence, both the covalency and ionicity will somewhat increase for the situation with B positioned in the second C layer of the diamond substrate.
4. Formation of graphene onto diamond (111) surfaces

4.1 Thermal-induced diamond-to-graphene formation

4.1.1 Graphitization of non-terminated diamond (111) surfaces in vacuum

The *ab initio* MD method has been used in simulating an annealing process for the diamond (111) surface. It is especially the temperature-induced diamond-to-graphene transformation that has been of interest to study. The initial diamond (111) surface model was non-terminated (see Fig.4.1) Within the present thesis, the annealing process was assumed to take place at strict vacuum conditions, and the temperature was set to 0 K, 500 K, 800 K, 1500 K, and 2000K, respectively. The total simulation time for each temperature was set to 0.3 ps, during which steady state conditions was achieved. The resulted structure of diamond (111) surface will thereafter be used as the initial structure for next MD simulation at higher temperature.

It is important to point out that a Pandey chain reconstructed diamond (111) surface, as shown in Fig. 4.2, is the first observation of surface structure evolution during the annealing process at around 800 K. As shown by earlier studies, the energy barriers at various extents are needed when transferring diamond (111)-1x1 to (111)-2x1\textsuperscript{68-69}. However, depending on different conditions, the energy barrier between these two local minima can be significantly changed. For example, it has been shown theoretically that the diamond (111)-1x1 to diamond (111)-2x1 transfer is associated with an energy barrier as low as 0.32 eV. However, for the situation with H-termination, the energy barrier will be as high as 58.4 eV\textsuperscript{70}.
Figure 4.1. Model showing the ideal diamond (111) surface that are used in simulating the surface structure evolution.

Figure 4.2. Demonstration of a Pandey chain reconstructed diamond (111) surface; a) side view, and b) top view.
The dynamic changes with temperature within the diamond (111) surface structure are shown in Fig. 4.4. With an increase in temperature from 500 K to 1000 K, the surface structure became Pandey Chain-reconstructed at a temperature of 800 K. At a higher temperature, it started to transform into graphene-like channels. When reaching a temperature of 1000 K, the breakage of C-C bonds within the second and third diamond C layer became more pronounced, thereby causing two parallel nearby-positioned Pandey chain reconstructed structures to merge together. The resulting channel-like structure had a width of 7 Å, and a height of 2.5 Å (see Fig. 4.3). By increasing the temperature to 1500 K, and even further to 2000 K, the graphene-like channels became even more pronounced since the number of C-C bonds within the interface decreased even further.

In summary, for the situation of an ideal diamond (111) surface, the temperature-induced structure evolution was observed to be a gradual and temperature-dependent transition from C-C bonds within the upper part of the diamond surface, to double bonds within the graphene-like adlayer.

![Figure 4.3. The structure evolution of a diamond (111) surface as a result of annealing from 0 to 2000 K](image)
4.1.2 H-induced graphitization

The graphitization process that was simulated in the previous Section was shown to take place at a high temperature. The final state of the simulated model was obtained to have a graphene-like adlayer at 2000K (i.e., graphene like channels were formed, that were covalently binding to the diamond surface. Therefore, in order to achieve a completely developed monolayer of graphene, even higher temperatures are considered to be needed. However, an interesting observation was made when studying the temperature-induced variations in the surface structure. The processes of breakage and recombination of bonds were concentrated to the interfacial region between the diamond surface and the graphene adlayer. In order to explain the reason for this phenomenon, the radical reactivity was analyzed by performing Fukui function, \( f(0) \), calculations (i.e., showing the interfacial susceptibility towards a radical attach) for the diamond (111) surface. The result of these calculations is shown in Fig. 4.4. The model shown in Fig.4.4 is at steady state at the temperature of 1500K. The radical sites, which are illustrated as blue “bubbles”, are mainly distributed in the newly formed surface layer of the diamond substrate, rather than within the graphene-like layer. It can thereby be concluded that the graphene-like adlayer is more stable than the underlying diamond surface layer. This is most probably due to the recombination of dangling bonds to \( \text{C} = \text{C} \) bonds within the graphene-like sheet.

![Figure 4.4](image.png)

*Figure 4.4. Radical reactivity calculated by using the Fukui function, \( f(0) \), method. The “bubbles” represent the sites that are susceptible for a radical attacked.*
Due to this result, H radicals were introduced into the model for further investigations. It has been experimentally shown that the H-terminating species will be thermally desorbed from the diamond (111) surface at a temperature range of 900-1200K under UHV conditions. Therefore, the temperature for the thermal-induced diamond-to-graphene formation, including H-radical species, was set to 1000 K in order to ensure the activity of the H radicals in the system. Surface structures, obtained from ab initio MD simulations at 1000 K, are in Fig. 4.5 shown for two situations: without and with one gaseous H radical in the model. It is obvious that the introduction of H into the diamond lattice will significantly increase the number of bond breakages between the diamond surface and the graphene-like adlayer.

*Figure 4.5. Comparison of the upper diamond (111) surface evolution at 1000 K, with or without the existence of an H radical in the initial model.*

Since only one H atom (in the super cell) gave rise to this effect at a relatively low temperature (less than 1500K), several H radicals were added to the system. As expected, the graphitization process was accelerated at even lower temperatures. As shown in Fig.4.6, when the diamond surface
was saturated with H, the addition of two extra H radicals (as shown in yellow color in Fig. 4.6) made the last covalent bonds between the graphene and diamond surface, to break at a temperature of 1000K.

4.2 Effect of an Fe interlayer on the epitaxial formation of graphene on a diamond (111) surface

4.2.1 Structural geometries

As discussed in Section 4.1., the transformation from diamond (111) to graphene requires a more or less high temperature in order to break the bonds. Besides the technique to introduce H radicals into the system, there is also the possibility to use metal catalysts in the graphene formation process. It has experimentally been shown possible to transform diamond (111) to graphene by using an fcc iron interlayer. In this part of the Thesis, the effect of an Fe interlayer, on graphitization process of diamond (111) surface, will be discussed. As a result of the experimental annealing process, the following geometrical model structure has been used in the present thesis for the analyzing the layer effect of Fe with DFT calculations (see Fig. 4.7). However, the number of Fe atomic layers has been varied.

![Figure 4.7. Formation of graphene onto diamond (111) in the presence of Fe as an interlayer material.](image)

In fact, different thicknesses (2, 3, 4 and 5 atomic layer) of the Fe interlayer were used, with the purpose to study the energetic stability of the diamond//Fe and Fe//graphene interfaces as a function of Fe interlayer thickness. The top views of the various diamond//Fe//graphene are shown in Fig. 4.8, and the side views are shown in Fig. 4.9.
Figure 4.8. Top view of the optimized structures for different atomic layers of Fe; a) 2, b) 3, c), 4 and d) 5 layers, respectively. The carbon atoms within the graphene layer, in addition to the first and second layer of the diamond surface are visualized in green, red and pink, respectively. The upper Fe atoms that are in contact with graphene, are shown in blue colour, and the lower Fe atoms that are in contact with the diamond substrate, are shown in light blue colour.

Figure 4.9. Side views of geometry optimized diamond//Fe//graphene structures with different atomic layers of Fe; a) 2, b) 3, c) 4, and d) 5 layers, respectively. The green layer denotes graphene, while the dark blue atoms indicate the upper Fe atoms (closest to the graphene layer). The light blue atoms indicate the lower positioned Fe atoms that are closest to the diamond slab. The red and pink atoms represent the first and second layer of diamond.
In Fig. 4.8, it can be seen that the carbon atoms within the graphene layer prefer to sit on top of the Fe atoms. This is also the situation for the diamond C atoms. However, there is a minor exception for the situation with a 3 atomic layer thick Fe interlayer. As can be seen in Fig. 4.8, the orientations of the graphene//Fe and Fe//diamond interfaces are slightly shifted from the strict on top positions towards a bridge position. Furthermore, due to this otherwise strict ontop positioning of C (diamond or graphene) versus Fe, the orientation of $C_{\text{graphene}}$ with respect to $C_{\text{diamond}}$ was observed as depending on the number of Fe layers (see Fig. 4.9). Therefore, for a 2, 3 or 5 atomic thick Fe interlayer, the C atoms within graphene are binding ontop the Fe atoms, which in turn have a hollow positioning with respect to the first atomic carbon layer of the diamond surface. Finally, a multilayer with 4 Fe atomic layers was found to be the only one for which the graphene carbon atoms were positioned right above (i.e., ontop of) the diamond surface carbon atoms.

### 4.2.2 Interfacial adhesion energies

The adhesion energy between the different layers is a factor used to indicate the degree of stability of a multilayer system. In order to study the effect of the Fe layer thickness on the diamond//Fe//graphene stability, the adhesion energies for graphene onto Fe//diamond, and graphene//Fe onto a diamond surface, have been calculated and analyzed.

As can be seen in Figure 4.10, the adhesion energies for graphene attached to diamond//Fe were found to be slightly more negative with increasing thicknesses of the Fe interlayer. There was otherwise a linear correlation between adhesion energy and Fe layer thickness. Hence, the binding between Fe and graphene became stronger for a thicker Fe interlayer. For the situation with a two atomic layer thick Fe interlayer, the adhesion energy was thus the lowest, -0.109 eV/atom. The strongest binding was observed for a 5 atomic layer thick Fe interlayer; -0.127 eV/atom. However, for the situation with a three atomic thick Fe interlayer, the minor shift from an ontop towards bridge position structure (see Fig. 4.8b), had an effect also on the adhesion energy (-0.122 eV/atom). However, it must be stressed that the adhesion energies for graphene attached to the Fe surface, are very low, and similar, for the various Fe thicknesses. On the other hand, the adhesion energies for an attached graphene//Fe layer onto the diamond surface, were observed to decrease with an increased Fe layer thickness; from -1.29 (2 layers of Fe) to -1.13 eV/atom (5 layers of Fe). Furthermore, it is clear that the interaction between the graphene//Fe and diamond surfaces is much stronger than the one between graphene and Fe//diamond.
Figure 4.10. Calculated adhesion energies (per carbon atom) for a) graphene attached to diamond//Fe (circles), and b) Fe//graphene attached to diamond (111) (triangles).

Figure 4.11. Bond distances between Fe and C (graphene) (circles), and between Fe and C (diamond) (triangles).

Figure 4.11 is demonstrating the change in C-Fe bond length with different thickness for the Fe interlayers. It must be stressed that the calculated Fe-C distance was equal to the distance between those layers since the Fe atoms were observed to reside ontop of the carbon atoms, as shown in Figure 4.8.
Furthermore, the $C_{\text{diamond}}$ – Fe distances have been found to be in strong correlation with the adhesion energy between the diamond and the Fe/graphene layers, (see Figs. 4.10 and 4.11). The variation in bond length and adhesion energy is most probably due to the quantum size effect, which is a phenomenon that will be analyzed in more detail in the Section below.

4.23 Electronic structures of the multilayer system

The calculated electron density difference map will indicate the changes in the electron density distribution when the individual atoms are forming the model system. The resulting electron density differences in the present Thesis, is shown in Fig. 4.12, The colored part of the electron density difference maps represents the electron gain (i.e., bond formation) within the system. On the left side of Fig. 4.12, the distribution of the electron density difference indicates an overlap between the non-paired electrons (i.e. dangling bond) on $C_{\text{diamond}}$ and the d-orbital within Fe. On the right-hand side of Fig. 4.12, the interactions between graphene and the Fe interlayer are shown to be even weaker (light green). Moreover, this interaction seems to be the result of an overlap of d-orbitals (within Fe), and the $\pi$ bonds of graphene. The strengths of these two interactions ($C_{\text{diamond}}$/Fe and Fe/C_{graphene}), as shown in Fig. 4.12), provide a visualized picture of the bond strengths which is strictly correlating to the adhesion energies shown in Fig. 4.10.
In addition to the electron density difference calculations, Density of State (DOS) calculations have been performed with the purpose to visualize the electron distribution with respect to the energy. The partial DOS for the adsorbed graphene adlayer can be seen Fig. 4.13a. It is clear that at an
energy level of 0 (the Fermi level), electron conductivity can be found for all graphene adlayers in the present Thesis. Furthermore, by increasing the thickness of the Fe interlayer, the DOS close to the Fermi level of the graphene layer, are slightly shifted towards higher energies. The same trend was also observed for the diamond substrate model with the presence of a five atomic thick Fe layers, which showed an increased intensity close to the Fermi level at the energy of -1 eV. However, no major difference between the pDOS spectra was observed for the graphene layer and diamond substrate, for the thinner Fe layers (i.e., two, three, and four atomic Fe layers). The pDOS spectra for the Fe interlayer are shown in Fig. 4.13c. As can be seen in this figure, as the Fe interlayer thickness increased, the DOS of Fe became concentrated around the Fermi level. The underlying reasons for this observation are most probably twofold. One explanation is the quantum size effect of Fe, which for this situation is one-dimensional (i.e., the Fe adlayer is only varied in the z-direction, while it infinite in the x- and y-directions). The second factor is the interaction with both the diamond substrate and the graphene adlayer. It is well-known that the formation of an interface will affect the DOS spectra for both surfaces that are involved in the interface, and therefore result in a shifted and/or broadening in the respective pDOS peaks. This circumstance is here clearly demonstrated for the diamond (111) surface (see Fig. 4.13a), and for the graphene adlayer (see Fig. 4.13b).
Figure 4.13. The partial density of states (pDOS) for a) graphene, b) the diamond (111) surface, and c) the Fe interlayer for various numbers of Fe atomic layers.
Density functional theory calculations for various diamond surfaces, with respect to different surface terminations and dopants, have been presented in the present Thesis. In addition, an *ab initio* Molecular Dynamic method has been used to study structural surface evolutions at various temperatures. The main purpose was to gain a deeper knowledge about how surface modification of diamond will affect its properties.

In **Paper I**, it was shown that the dopants (N and B) will affect the surface geometrical structure. With the results of adsorption and relative (in relation to H-termination) stabilization energy calculations, for differently terminated diamond (100) surface, the order of stability was obtained as $O_{\text{bridge}} > O_{\text{ontop}} > H > OH$. However, the existence of N (or B) dopants was observed to give more positive stabilization energy. In practise this means that these specific dopants will induce a decrease in the stability of the diamond surface. For an H-terminated diamond surface, the analysis of atomic charges and bond population indicated that the dopants will either donate partial electron density to the antibonding states of the C-H bonds (for N doping), or withdraw partial electron density from the C-H bonding states (for B doping). For both situations, the C-H bonds in the vicinity of the dopant will be weakened. For an O-terminated diamond surface, it was found that the N dopant enhances the neighbouring C-O bonds by donating its extra electron. For B doping, the C-O bonds in the vicinity of the dopant were found to be weakened by sharing electron density with B, which has one less electron comparing to carbon. In addition, pDOS calculations indicated a strictly localized electronic conductivity for a 100% $O_{\text{ontop}}$ coverage.

The possibility to use B-doped diamond in a dye sensitized solar cell was investigated in **Paper III**. The effect of substitutional positioned B dopant on the adsorbed dye molecules, were thereby investigated. The result clearly showed that with B positioned in the 2nd atomic layer, the bonding of the dye molecule to the diamond surface was stronger than for the situation with B positioned in the 3rd atomic C layer. In addition, the degree of electronic transfer from the diamond surface to the dye molecules became more pronounced. More importantly, the DOS spectra provided strong evidence for a splitting of the frontier orbitals, or a decrease in the HOMO-LUMO gaps of the adsorbed sensitizers. The decrease in band gap will facilitate a more efficient absorption of visible light.
The temperature-induced structural evolution of the diamond (111) surface was investigated in **Paper II**. This annealing process was simulated by using an *ab initio* MD method. A graphene-like adlayer, that was bound to the diamond surface in the form of channels, was formed at a temperature of ~2000 K. Due to the observation of reactive radical C sites at the interface of the graphene-like and the newly formed diamond surface, H radicals were introduced to the interface in the annealing process. As a result, the H radicals were found to be efficient in the breakage of the C-C bonds, and the temperature needed to form the graphene-like layer could be dramatically decreased. In addition, by completely saturating the radical C atoms with H radicals, a free-standing graphene layer was formed at a temperature of 1000K. Moreover, the effect of an Fe interlayer on the diamond-to-graphene formation was investigated in **Paper IV**. Various thicknesses of the Fe slab (i.e., 2, 3, 4 and 5 atomic Fe layers) were thereby used. Geometrically, C\textsubscript{graphene} on top of Fe, and Fe on top of C\textsubscript{diamond} were observed for all different situations. The calculated adhesion energies for the situations with i) graphene on top of Fe//diamond, and ii) graphene//Fe on top of the diamond substrate, were found to be in the range i) -0.109 to -0.127 eV/atom, and -1.29 to -1.13 eV/atom, for the various Fe thicknesses. As a support to these numerical results, the electron density difference maps visualized the binding conditions within the interface for the various Fe interlayer thicknesses. As a conclusion, the graphene was observed to bind to Fe interlayer by very weak electrostatic bonds, while the bonds between the Fe interlayer and the diamond surface was of a covalent nature. Moreover, the visualized pDOS spectra showed a more pronounced electron density close to the Fermi level for both the diamond substrate and the graphene adlayer. By comparing these pDOS spectra with the one for the Fe interlayers, the conclusion is i) that the Fe slab shows evidence of a one-dimensional quantum size effect for these small thicknesses, and ii) the broadening or shift of the peaks close to the Fermi level is a consequence of the binding states over the interface.
Diamant är ett unikt kubiskt material med utomordentliga material-egenskaper. Som resultat av ett mångårigt utvecklingsarbete inom gasfas-deponering av diamant, så kan man numera deponera tunna diamant-filmer med önskad dopningsgrad, samt ytmodifiering. Diamant har därmed kommit att bli en stark kandidat för tillämpningar baserade på elektrokemi, samt elektronik. Diamant här även under de senaste åren visat sig utgöra ett suveränt material inom bioteknologin.

Materialet grafen utgör en annan polymorf form av kol, vilket har visat sig äga många excellenta egenskaper. Grafen är ett hexagonalt material, vilket i princip utgöres av ett, eller några få, atomära C lager av grafit. Emellertid, för att till fullo utnyttja detta material inom flertalet viktiga tillämpningar, så återstår utmaningen att kunna syntetisera högkvalitativ grafen på större yta.

Beräkningar med hjälp av densitetsfunktionalteori (DFT) har använts för att förutsäga hur diamantytor påverkas av olika yttermineringar och dopningsämnen. Dessutom så har ab initio molekyldynamik (MD) använts för att studera förändringar i morfologin som funktion av temperaturen. Det huvudsakliga syftet var att få en djupare kunskap om hur olika förändringar av diamant och dess yta kommer att påverka egenskaperna för detta material.

I Paper I, visades hur dopämnen (N och B) påverka ytstrukturer (dvs. Csurface-X, där X är Obrygga, Oovanpå, H och OH), bindningslängder och vinklar till de omgivande atomerna. Från resultaten av adsorptions- och relativa (i förhållande till adsorberad H) stabiliserings-energin kom man fram till följande stabilitetsordning; Obrygga> Oovanpå> H> OH. Vidare observerades att dopämnena N och B minskade stabiliteten av kol på ytan jämfört med en odopad diamantyta.

För en H-terminerad diamantyta visar beräkningarna av de atomära laddningarna, och fördelningen av elektroner i bindningarna C-H, att dopämnenan antingen donerar elektroner till de antibindande tillstånden (N-dopning) eller minskar den partiella elektronfördelningen från de bindande tillstånden (B-dopning). I båda situationerna kommer C-H bindningarna i närheten av dopämnet att försvagas. För en O-terminerad diamantyta, visade det sig att dopning med N förstärker C-O bindningen genom att donera sin extra elektron.

För B-dopad diamant försvagades C-O-bindningen i närheten av dopämnet genom att dela en elektron med B som har en elektron mindre än
C. Dessutom så visade pDOS-beräkningar en mycket hög elektrisk ledningsförmåga på ytan för 100% täckningsgrad av Oovanpå.

I papper III undersökt möjligheten att använda färgämnessensiterade solceller av B-dopad diamant. Speciellt undersöktes effekterna av hur substitutionellt B påverkade de adsorberade färgämnessmolekylerna. Resultatet visade tydligt att med B placerat i det andra atomlagret under diamantytan så blev bindningen C-färgämnesmolekyl starkare. Detta medför att överföringen av elektroner mellan diamants yta och förgämnet förbättras och att ljusabsorptionen som kan ge laddningsbärare ökar.

Temperaturens inverkan på ytstrukturen hos en diamants (111)-yta, undersökt i papper II. Värmebehandlingen simulerades med ab initio MD. Ett grafenliknande ytlager i form av kanaler bildades på diamantytan vid temperaturer över 2000 K. Eftersom reaktiva platser uppstod i gränsskiktet mellan det grafenliknande ytlaget och diamantytan, testades att införa H-radikaler. Dessa radikaler visade sig vara effektiva att bryta C-C-bindningarna i gränsskiktet, och ett helt fristående grafenlager kunde nu bildas redan vid 1000 K.

Effekten av Fe i gränsskikted diamant - grafen undersökt i Paper IV. Olika tjocklekar av Fe (2, 3, 4 och 5 atomlager) användes.

Rent geometriskt användes konfigurationen C_{graphene} ovanpå Fe och Fe ovanpå C_{diamant} i alla beräkningarna. Adhesionsenergierna från i) grafen ovanpå Fe//diamant och ii) grafen//Fe ovan på diamant beräknades för 2-5 atomskikt av Fe. Konstruktion och analys av en elektrondifferenskarta visade att grafen bands till Fe med mycket svaga elektrostatiska bindningar medan bindningen mellan Fe och diamantytan var mer kovalent till sin natur. Dessutom så visade analysen av elektronstrukturen en högre elektrondensitet nära Fermi-nivån för både grafen och diamant.

Genom att jämföra pDOS –spektra från atomlagren av Fe så kan följande slutsatser dras:

i. Järnlagren visar upp en endimensionell kvantstorleksbefattning och
ii. Breddningen av topparna nära Fermi-nivån är en konsekvens av bindningsförhållandena i gränsskiktet.
7. Acknowledgement

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8. References


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