The Effect of Various Dopants on Diamond Growth

A Combined Experimental & Theoretical Approach

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Abstract

Diamond is a unique material with many exceptional properties. It has therefore been proven to be an important material for many applications. Moreover, the introduction of dopant species into the gas phase during the CVD growth process has been shown to strongly influence not only the properties and morphology of diamond, but also the growth rate. The purpose with the theoretical part of the present study has been to support and explain the experimental observations regarding the effect of various dopants (nitrogen, phosphorous, sulphur, and boron) on the diamond growth rate. Commonly observed H-terminated diamond surfaces [(111), (110) and (100)-2×1], were thereby carefully investigated using density functional theory under periodic boundary conditions. Based on the assumption that the hydrogen abstraction reaction is the growth rate-limiting step, both the thermodynamic and kinetic aspects of the diamond growth process were found to be severely affected by various dopants. More specifically, the results showed that nitrogen and phosphorous dopants (positioned within the 2nd, 3rd or 4th carbon layer) will cause an enhancement in the growth rate (as compared with non-doped situations). On the other hand, any growth rate improvement does only occur when positioning boron in the 2nd, and sulphur in the 4th, atomic carbon layer. With boron, and sulphur, positioned within the other atomic carbon layers, the growth rates were observed to decrease. In addition, the main purpose with the experimental part of the present study has been to investigate the effect of one specific dopant precursor (TMB) on the boron-doped diamond growth process. The result has shown that the increasing mass flow of TMB will not affect the mechanism of the HFCVD growth process of boron doped diamond. However, a linear boron carrier concentration in the diamond film vs. mass flow rate of TMB was observed.

Keywords: Diamond, Growth rate, HFCVD, Doping, Activation energy, Reaction order

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To my wife and parents
List of Papers

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


II Zou, Y., Larsson, F., Larsson, K. Effect of Sulphur and Phosphorous Doping on the Growth Rate of CVD Diamond (111). *Submitted*.

III Zou, Y., Larsson, K. Effect of Boron Doping on the Growth Rate of CVD Diamond. *Manuscript*.

IV Zou, Y., Boman, M., Larsson, K. Effect of TMB on the HFCVD Boron Doped Diamond. *Manuscript*.

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The author also contributed to the following papers, which are not included in the present thesis:


My contribution to the included papers

I contributed to the design of the work, and performed the majority of the calculations. I also contributed to the writing of the manuscript.

II contributed to the design of the work, and performed most of the calculation. I did most of the writing of the manuscript.

III contributed to the design of the work, and performed all calculations. I did most of the writing of the manuscript.

IV contributed to the design of the work, and performed all experimental work. I did most of the writing of the manuscript.
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## Abbreviations

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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<td>HPHT</td>
<td>High Pressure High Temperature</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<td>HF</td>
<td>Hot Filament</td>
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<td>DFT</td>
<td>Density Functional Theory</td>
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<td>LDA</td>
<td>Localized Density Approximation</td>
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<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
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<tr>
<td>SCCM</td>
<td>Standard Cubic Centimeter per Minute</td>
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<tr>
<td>TMB</td>
<td>Trimethylborate</td>
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<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<td>MSP</td>
<td>Mott-Schottky Plot</td>
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<td>MWPA</td>
<td>Micro-wave Plasma Assistance</td>
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1. Introduction

1.1 Diamond

Diamond has many excellent physical and chemical properties due to its crystalline structure with four equivalent bonds between sp³ hybridized carbon atoms (see Figure 1). Due to its low natural abundance in nature, it has a very high commercial value as a gemstone. However, natural diamond has been found not to be appropriate for industrial applications. After that diamond was first successfully synthesized in 1879 [1], its industrial value has become quite interesting as a thin film, or coating on another material. For instance, it’s very high hardness, low coefficient of thermal expansion and friction [2] make diamond suitable for the machining and cutting of hard materials. Other properties of diamond, such as transparency of light from UV regions to the far IR, make diamond useful for transmission windows and domes [3]. Diamond can also be used as a thermal conductor (e.g., for high-power transistors and as a heat sink for laser diodes). This will prolong the lifetime of electronic devices that are dependent on high thermal conductivity [4]. In addition, diamond is chemically inert, which makes it useful for application in aggressive environments. Despite the large band gap of diamond (i.e., about 5.45 eV), it is always considered as an insulator. However, the possibility of doping with various dopants make diamond exhibits extraordinary electronic properties, such as high carrier mobility. In addition to the wide electrochemical window [5], the diamond material thereby became recently a promising candidate for application in various type of electronic devices [6]. Most recently, it has also been found that diamond is compatible with biological tissues [7] which opens up the application of diamond in biomedical applications [8]. However, to be successful with the implementation of diamond in these applications, further development of the growth process of synthetic diamond (on various substrates) has to be fulfilled.
1.2 Synthesis of diamond

Since the beginning of the 19th century, the development of diamond synthesis has been highlighted by using two major types of synthesis methods; a High Pressure High Temperature (HPHT) method and a Chemical Vapor Deposition (CVD) method. By using the HPHT method, a high temperature (1700-2000K) and a high pressure (70-80kPa) are used to simulate the earth core environment where natural diamond is being synthesized [9]. For lower temperatures and pressures, there will be a phase transformation to graphite [10]. By using the CVD method, diamond was very early observed to deposit onto a substrate surface by using gaseous precursors (as introduced by William Eversole in 1952) [11]. These precursors form various types of fragments (i.e., C-containing species and hydrogen radicals) when activated by hot filament (HF) or plasma [12]. The mostly used precursors are hydrocarbons (i.e., CH₄) coupled with a super-saturation of hydrogen molecules. The role of the hydrocarbons is to provide C-containing species, and the role by the hydrogen radicals is either to ensure the continuation of an sp³-hybridized surface C atoms (i.e., by etching the graphite formed on the diamond surface), or to react with the C-containing species to form predominantly CH₃ radicals [13]. This CVD method has become a very versatile method developed during the latest decade. As compared with the HTHP method, the CVD synthesis process takes place within a lower temperature range (800-1100K) and at a lower pressure (0.6-1.4kPa). Furthermore, the
diamond produced by using the CVD method is better controlled when it comes to gas phase content and minimization of impurities. In addition, large area diamond films can be deposited [14]. Thus, commercialized CVD diamond products are quite common nowadays because of their high purity and quality. However, both of these two methods (i.e., HF CVD and plasma activated CVD) are quite expensive for the growth of diamond. It is thereby very important to reduce the production costs, which can be done by either improving the growth rate, or by decreasing the temperature.

1.3 Doping of diamond

Doping of diamond can be performed by introducing impurities into the diamond structure and thereby modifying the properties of the diamond material. The most important dopants are nitrogen, boron, phosphorous and sulphur, which all will be substitutionally incorporated into the diamond lattice. The dopants will not only change the electronic properties, but it is also clear that these dopant elements can have a great impact on the diamond surface morphology and growth rate. It is believed that the enhancement of the diamond growth rate will thereby reduce the production cost. By using the CVD method, it is very convenient and well-controlled to add a specific dopant concentration into the diamond lattice during the growth process. Thus, the effect of dopants on the diamond growth rate will be mainly investigated and discussed in the present thesis.

1.3.1 Nitrogen doping

For the situation with nitrogen doping into the diamond lattice, it will induce a level in the band gap 1.7 eV [15] below the lower conduction band edge, which makes diamond an n-type semiconductor. This electronic level is too low to be able to use diamond in devices at room temperature[16]. However, it is still an important type of doping since it has been experimentally proven that the presence of nitrogen in the gas phase will strongly influence the growth rate [17]. This influence (i.e., enhancement of diamond growth rate) has been reported for both poly- and mono-crystalline diamond [18-20]. It has recently been observed, by using laser reflection interferometry, that when the gaseous nitrogen concentration in the reactor is as low as a few ppm, the crystal growth rate in the (100) orientation will be strongly improved. [21].

However, it is experimentally very difficult to acquire knowledge about the underlying causes to the observations made by nitrogen doping. Bar-Yam and Moustakas [22] did propose a defect-induced stabilization of diamond, but they could not explain the orientation (i.e., planes) dependence of the increasing growth rate. In addition to the vast number of experimental
work in this area, there are also some theoretical studies performed in order to find the underlying effect by nitrogen to the diamond growth rate. For example, Frauenheim et al. [23] suggested that the extra valence electron (i.e., as compared to the carbon atom) in nitrogen will be transferred to a (100) surface reconstruction bond, and thereby lengthening this bond. Reactive adhesion sites for a gaseous CH$_2$ may thereby be created [23, 24]. However, their calculations are limited since the concentration of gaseous CH$_2$ is actually very low during growth.

1.3.2 Boron doping

The boron atom can also be easily substitutionally positioned within the diamond lattice. However, different properties can be achieved depending on the doping level. This type of doping has therefore been of a large interest to study during the last decade. At low boron doping concentrations, a p-type semi-conductor will be obtained with an initially empty state positioning 0.4 eV above the upper valence band edge [25, 26]. At higher boron concentration, the doped diamond will show metallic-like conductivity [27, 28]. This kind of extrinsic conductor properties widen the usage of diamond, such as for applications in the areas of wastewater treatment [29], electro synthesis [30] and electro analysis [31]. Boron doped diamond has become even more attractive for electronic applications when superconductivity has been reported [32]. These electronic properties of boron doped diamond are completely different as compared with intrinsic diamond. When using the CVD method, this type of dopant does also show a great impact on the diamond surface morphology and growth rate [33-36]. In those experimental studies, both a decrease in growth rate, as well as a slightly increase, has been observed at a very low boron concentration in the gas phase [37]. In addition, Wang [38] and Haubner [39] have found that an increase in growth rate can be obtained at different temperatures and pressures.

The reason for the different effects by boron on the growth process has not experimentally been fully understood. It has been concluded that the decrease in growth rate is related to the low nucleation rate when boron has been introduced during the growth process. [33-36]. Theoretical studies have been performed in order to investigate the electron properties [40-42], especially for the reason of superconductivity [43, 44]. However, few studies [45, 46] have focused on the growth mechanism. Those few theoretical studies have only focused on the boron incorporation mechanism into the diamond lattice. The effect by boron on the initial diamond growth process (i.e., hydrogen abstraction from an adsorbed CH$_3$) was initiated by Van Regemorter [47], who assumed that the diamond surface during growth is partially terminated with BH$_2$ groups.
1.3.3 Phosphorous doping
Since phosphorous, as the same as nitrogen, has one more valance electron as compared to carbon, it can also transform diamond into an n-type semiconductor (i.e., with an induced level at 0.6 eV below the conduction band). After that Koizumi et al. [48] managed to incorporate phosphorous into the diamond lattice, the first diamond-based p-n junction material (as a light-emitting diode) was constructed [49]. Although the utilization of phosphorous doped diamond as a new n-type semiconductor material has not been quite developed, there have already been a lot of studies that focus on the properties of such phosphorous doped diamond materials. [50-53]. In addition, the effect by phosphorus on the diamond growth rate has also been reported [54, 55]. S. Bohr et al. has made a great effort in this direction [56]. They investigated the effect of different phosphorus concentrations (within a PH₃/CH₄ gas mixture) on the growth rate, and on the surface orientation of CVD diamond. Their results show a great impact of phosphorous doping on the increasing diamond (111) growth rate. As was the situation with the nitrogen- and boron-doping scenarios, there are some theoretical studies considering the influence by the phosphorous dopant on the diamond properties [40, 57]. One report states that the high energy associated with phosphorous induced strains will affect the diamond growth rate [45]. However, many questions still remain unanswered.

1.3.4 Sulphur doping
Another type of n-type diamond semiconductor material was initially achieved by M. Hasegawa et al. by using sulfur-ion-implantation in homoepitaxial diamond (100) films [58]. After these initial results, sulphur doping of diamond has been widely investigated for their electronic properties [59-61]. In addition to the effects on the electronic properties, the effect by sulphur on the growth rate has also been investigated. Most of the experiments have shown a dramatic decrease in growth rate [60, 62], but Sternschulte et al. did also find the possibility to increase the growth rate by varying the temperature [63]. They tried to explain the effect by sulphur incorporating by the fact that it is adsorbed sulphur that causes the enhancement in growth rate, whilst the decrease in growth rate is strongly caused by the reduction of diamond nucleation with the addition of H₂S. Some theoretical studies have focused on sulphur doped diamond in the attempt to help the experimentalists to understand the n-type semiconductor properties [64, 65]. The effect by sulphur on the CVD diamond growth mechanisms has theoretically been studied by Tamura et al [66]. They concluded that sulphur will enhance the hydrogen desorption process from the surface. However, the
underlying causes by the sulphur doping effect on the growth rate, is not yet fully investigated.

### 1.4 Initial growth step within CVD of diamond

The growth of CVD diamond is a very complex and dynamic process [67]. Since the growing diamond surface will otherwise collapse to the graphitic phase, the growing diamond surface has to be terminated with hydrogen atoms. However, these hydrogen terminations must be abstracted away from the surface to explore a reaction site and leave room for a growth species (e.g., CH₃). This is the initial step of the diamond growth process before any surface adsorption, or migration, can take place. Hence, the hydrogen desorption from the diamond surface (i.e., hydrogen abstraction) is one of the important and fundamental reaction steps during the overall diamond growth process [68]. The hydrogen abstraction reaction is activated by gaseous radical hydrogens in the gas phase:

\[
C_{\text{diamond surface-H}} + H• \rightarrow C_{\text{diamond surface•}} + H_2
\]

where \(C_{\text{diamond surface-H}}\) is the hydrogen-terminated surface, \(C_{\text{diamond surface•}}\) is the resulting activated surface site, \(H•\) is the hydrogen radical, and \(H_2\) is the resulting hydrogen molecule. Since it has been reported that the hydrogen abstraction process is an endothermic reaction for non-doped diamond, whilst the adsorption of e.g. CH₃ is highly exothermic (+17 vs. -348 kJ/mol) [69], the theoretical studies in the present thesis are based on the assumption that the hydrogen abstraction is one of the rate-limiting steps for the diamond growth process.

### 1.5 Aim of the thesis

The main purpose of the present thesis has been to learn as much as possible about the effect of either n- or p-type doping on the diamond surface properties, and to develop the possibility for higher diamond CVD deposition rates. Therefore, the main methodology of the present thesis has been to investigate the effect by different dopants on the hydrogen abstraction process from an otherwise completely H-terminated diamond (111), (110) and (100)-2×1 surface, respectively. Especially, the enhancing effect by nitrogen doping on the diamond (100)-2×1 growth rate has been theoretical explained and found to strongly support recent experimental observations (Paper I). Moreover, the effect by phosphorous and sulphur doping for the highly symmetric diamond (111) surface has been theoretical investigated from both a thermodynamic and kinetic point of view (Paper II). In addition, the influence by the
boron dopant on the diamond growth rate has been analyzed at an electron level while calculating the hydrogen abstraction energy and energy barrier (Paper III). Moreover, an experimental Paper IV has been focused onto the effect of boron dopant on the diamond morphology and growth, where different boron concentrations in the gas phase, and different substrate temperatures, have been used.
2. Theoretical methods and models

2.1 General
All theoretical calculations in the present thesis have been performed with Density Functional Theory (DFT), which is an ab initio method. This method is one of the most widely used theoretical approaches and has been developed tremendously during the last decades. An electron density distribution is used in the DFT calculations to simulate various materials and their properties. It is thereby regarded as one of the most accurate calculation techniques.

2.2 Density Functional Theory
The many-body system can be described by solving the time-independent Schrödinger equation, as follows:

\[ H\Psi = E\Psi \]  
Eq.1

where \( H \) stands for the Hamiltonian operator, \( \Psi \) is the many-electron wave function and \( E \) is thereby the obtained total energy [70].

The Hamiltonian operator is dependent on the kinetic energies of nucleus and electrons, the Coulomb potential for electron-nucleus interaction, electron-electron repulsive interaction, and nucleus-nucleus repulsive interaction. The Hamiltonian operator can thereby only be exactly solved for one-electron systems such as \( H \) and \( \text{He}^+ \). For more interesting many-particle systems (i.e., molecules, surfaces), approximations have to be incorporated in the Hamiltonian expression. Thus, the Born-Oppenheimer approximation has been used, where the much lighter and faster electrons (i.e., compared to nuclei) are treated as if they are moving in the field of fixed nuclei [71]. With this approximation, the total wave function within the Schrödinger equation will be separated into \( \Psi_e \) (i.e., describing the electron behavior) and \( \Psi_N \) (i.e., describing the nuclei behavior).

For the electronic part of the wave function, \( \Psi_e \), Hartree has introduced another approximation [72] in order to treat the total wave function for \( N \) electrons as a combination of independent single electron wave functions:
\[ \Psi_e(r_1, r_2, \ldots, r_N) = \psi_1(r_1)\psi_2(r_2) \ldots \psi_N(r_N) \quad \text{Eq.2} \]

where each of the functions \( \psi_N(r_N) \) is a one-electron wave function within the Schrödinger equation. Moreover, Fock has proposed to describe the total wave function with a Slater determinant [73]; the Hartree-Fock (HF) method, which is also called a “self-consistent” method [74]. Another approach for describing electrons is to use electron densities. This method, called Density Functional Theory (DFT), was first used to calculate molecular properties [75]. Within this method, the total energy of the system is expressed as:

\[ E[\rho] = T[\rho] + E_{eN}[\rho] + E_{ee}[\rho] + E_{xc}[\rho] \quad \text{Eq.3} \]

where \( T \) is the term of kinetic energy, \( E_{eN} \) and \( E_{ee} \) are the nuclear-electron attraction and the electron-electron repulsion, and \( E_{xc} \) is the exchange-correlation energy. By expressing the various terms as a function of the electron density, DFT can be used for larger systems and even extended to liquids and solids without the need to use more simple empirical data as input in the calculations [76]. However, the exchange-correlation energy term, \( E_{xc} \), is the problematic term since it cannot be calculated exactly for systems larger than, e.g., \( \text{H} \). There are many different types of approximations that have been developed for the purpose to find a proper description of the exchange-correlation energy. The Local Density Approximation (LDA) is the simplest approach where the electronic behavior is defined by a hypothetical uniform electron gas (see Eq.4). Thus, the \( E_{xc} \) can be calculated with a high accuracy for simple systems such as a homogenous gas and for simple metals. However, for the binding in semi-conductors and non-metallic materials, LDA has been shown to overestimate the bond strengths. The Generalized Gradient Approximation (GGA) has for these systems proven to work quite well. The gradient of the charge densities is thereby introduced in order to describe these more complex models [77] (see Eq.5). As compared to LDA, it has been shown that GGA provides a considerable increase in accuracy of the energy evaluations and geometry optimizations, especially for the diamond models in the presented thesis [78].

\[ E_{xc}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho) d\mathbf{r} \quad \text{Eq.4} \]

where \( \varepsilon_{xc}(\rho) \) is the exchange-correlation energy per electron as a function of a constant density \( \rho \) at position \( \mathbf{r} \) in the uniform gas.

\[ E_{xc}^{\text{GGA}}[\rho] = \int \rho(\mathbf{r})\varepsilon_{xc}(\rho, \nabla \rho) d\mathbf{r} \quad \text{Eq.5} \]
where $\epsilon_{xc}(\rho, \nabla \rho)$ is the exchange-correlation energy for each electron, as calculated by a non-local function that depends on the gradient of the density $\nabla \rho$ at position $\vec{r}$.

2.3 Models and parameters setup

The most frequently observed surfaces during CVD deposition of diamond thin films are the low Miller index planes (111), (110) and (100). Three different super cells, modeling the diamond surface planes, have therefore been used in the present thesis (as can be seen in Figure 2). For modeling the (100) surface, the (100)-2×1 reconstructed mono-hydride surface was used. In order to simulate an as-grown CVD diamond surface, the diamond models were terminated by hydrogen atoms. Moreover, periodic boundary conditions were used, with infinite models in the x- and y- directions, in order to better simulate the models as surfaces. In addition, a large vacuum distance between the slabs (i.e., in the z-direction) was used to eliminate non-realistic inter-slab interactions. The bottom layer of the diamond model was also H-terminated and constrained during the geometry optimization process. Thus, the dangling bonds of the bottom carbon atoms have been saturated and the continuation into bulk diamond has thereby been simulated. The rest of the atoms were allowed to freely relax by using the BFGS algorithm in the calculations [79].

In the incorporation of different dopants (i.e., nitrogen, boron, phosphorous, and sulphur) into the diamond lattice, the dopant was substitutionally positioned in either carbon atomic layer 1, 2, 3, or 4. Nitrogen was also attached to the diamond surface in the form of a radical NH, or NH$_2$ group.

The calculations were performed by using the CASTEP program (Accelrys, Inc.), which is based on an ultra soft pseudopotential under periodic boundary conditions [80-81]. In addition, the electron exchange correlation has been calculated by using the Perdew-Burke-Ernzerhof (PBE) function [77, 80]. Spin polarized methods were used for the investigation of models that involved unpaired electrons (e.g., doped diamond systems). The cut-off energy for the plane waves, and the k-points values in the reciprocal space, were both evaluated in test-calculations in order to minimize the computational time, and at the same time upholding a necessary accuracy for the various systems. Moreover, the construction of the models was also tested, and it was shown optimal to use a 4×4×6 supercell in the simulations of the hydrogen abstraction processes.
Figure 2. Representation of supercells for modeling three diamond surface planes: a) (100)-2×1; b) (110); and c) (111). One dopant was substitionally positioned within the different layers.

Figure 3. a) Representation of the diamond surface before and after hydrogen abstraction reaction; b) Illustration of the simulated hydrogen abstraction process.
2.4 Thermodynamics and kinetics calculations

As presented in Section 1.4 *Initial growth step within CVD of* diamond, it has been assumed that the hydrogen abstraction from the surface is a growth rate-limiting elementary reaction. This specific reaction has therefore been focused in the present thesis, from both a thermodynamic and a kinetic point of view. Thus, the influence by the dopant on the driving force for the hydrogen abstraction reaction has been highlighted as a thermodynamics study. In addition, the effect of the dopant on the hydrogen abstraction rate has been investigated by performing energy barrier calculations.

More specifically, the abstraction reaction takes place as a gas phase hydrogen abstraction of a surface terminating hydrogen species [see Reaction (1)]. The abstraction energy has thereby been expressed as:

\[
E_{abs} = (E_{\text{surface}•} + E_{H2}) - (E_{\text{surface}-H} + E_H) \quad \text{Eq.6}
\]

where \(E_{\text{surface}•}\) and \(E_{\text{surface}-H}\) are the total energies for optimized surface structures with one hydrogen atom abstracted and fully covered by hydrogen atoms, respectively (see Figure 3a). Moreover, \(E_{H2}\) and \(E_H\) are the total energies for gaseous \(H_2\) and \(H\), respectively. Thus, the effect by dopants on the thermodynamic driving force for the diamond growth rate has been investigated by abstracting the closest (or one of the closest) surface hydrogen atom relative to the dopant.

The energy barriers have been calculated by simulating the hydrogen abstraction process, where the gaseous hydrogen radical has approached a surface hydrogen atom. In this simulation, an hydrogen radical was initially positioned 4 Å above one of the most reactive surface hydrogen adsorbates, and was thereafter positioned towards the surface in smaller steps; from 4.0 Å to 1.0 Å, in steps of 0.2 Å (see Figure 3b). For each step, the introduced hydrogen radical was constrained during the geometrical optimization, and the energy barrier was thereby expressed as:

\[
\Delta E = E_{\text{maximum}} - E_{\text{furthest away}} \quad \text{Eq.7}
\]

where \(E_{\text{maximum}}\) is the energy at the transition state, and where \(E_{\text{furthest away}}\) is the energy of the system when the hydrogen radical is furthest away from the surface hydrogen atom (i.e., 4 Å). The effect of dopants on the kinetic energy barriers for the approaching hydrogen atom has thereby been investigated. Moreover, when the hydrogen radical was positioned closest to the surface-binding hydrogen species, a reaction between these two hydrogen atoms started to take place. As a second step in the hydrogen abstraction process, a step-wise removal of the hydrogen molecule was investigated. For these calculations, one of the hydrogen atoms in the hydrogen molecule was kept fixed during the geometry optimization process.
2.5 Property analysis methods

The population assignment of the atomic charge for a specific atom (e.g., the dopant), or for the bond population in a system (e.g., the C_{surface}–H bond), is widely used as an analysis method in understanding the electronic properties of the system. This population analysis has been performed by using the method of Mulliken analysis, which in turn is using a projection of the plane wave states onto the localized basis by a technique described by Sanchez-Portal et al [81]. As mentioned in Section 2.3 Models and parameters setup, spin polarized methods were used for the doped diamond models, where the alpha and beta spins have been described by different wave functions. Thus, with this kind of set up, the difference between these two charge densities gives the result of a spin density. Moreover, Fukui functions, as introduced by Fukui [82, 83], and later on modified by Parr [84] and Yang [85], are reliable in investigating surface reactivities. Thus, the susceptibility of an electrophilic, nucleophilic or radical attack to the surface can be calculated. For the purpose to indicate the surface reactivity towards a hydrogen radical attack (see Figure 3b), the radical Fukui function, defined as $f^0$ (see Eq.8), was mostly used in the present thesis.

$$f^0 = \frac{1}{2}(\rho_{N+\Delta}(r) - \rho_{N-\Delta}(r))$$

Eq.8

where $\rho_N$ is the electron density at a point $r$ in the space around the molecule, $N$ corresponds to the number of electrons in the molecule, $N+\Delta$ corresponds to an anion with an electron added to the LUMO of the neutral molecule, and $N-\Delta$ corresponds to an cation with an electron removed from the HOMO of the neutral molecule. In conclusion, the calculated atomic charges, bond electron populations, electron spin densities and radical Fukui functions have been very important tools in the interpretation of the underlying causes to the effect of dopants on diamond growth.
3 Experimental methods

3.1 General
All the diamond films were deposited onto Silicon (100) wafers by using a loadlock HFCVD reactor (model BWI 1000 HFCVD by Blue Wave Semiconductors). The HFCVD method was chosen because it is a well proven technique for growing diamond films over large areas. As compared to MW-CVD (micro-wave plasma CVD), the lower cost and the relative ease of scalability of HFCVD was considered advantageous for producing low cost thin films of diamond.

3.2 Precursors
As presented in Section 1.2 Synthesis of diamond, hydrogen plays a very important role in the diamond synthesis. Thus, hydrogen was introduced into the chamber though a mass flow controller (MFC). Moreover, methane (CH₄) was chosen as carbon precursor since it can produce methyl radicals which is propitious to diamond growth [86].

Trimethylborate (TMB, see Figure 4) has been used as the boron precursor. It is easily evaporated due to the high vapor partial pressure at the room temperature [87] and the gas flow can be measured through a mass flow controller. Another advantage is the low toxicity and reactivity of trimethylborate compared to the different boranes. Solid precursors have also been used as a boron source because of the higher safety. It is well-known that solid boron substances such as oxides are nontoxic. The boron trioxide (B₂O₃) powder can be sublimated and added and mixed with other gaseous reactants during the diamond growth [88]. Solid precursors are, however, difficult to evaporate which reduces the reproducibility of the CVD process. Dissolving B₂O₃ powder into an organic solvent was first used by K.Okano et al [89], the boron/carbon ratio then can be varied by changing the quantity of, in this case, acetone. This method has the advantage that liquids can be used which is much easier to control resulting in a more reproducible CVD process. These borate liquid sources can be introduced to the reaction chamber though MFC using hydrogen as carrier gas. Generally, the boron doping level is qualitatively determined by the carrier H₂ flow rate [90]. More spe-
specifically, the flow rate of boron source can be approximately determined by the Dalton partial pressure law as:

\[ F_{\text{boron}} = \frac{p_{\text{borate}}}{p_{\text{total}}} \times F_{\text{total}} \]  

Eq. 9

where \( p_{\text{borate}} \) is the partial pressure of the borate liquid source, \( p_{\text{total}} \) and \( F_{\text{total}} \) are the total pressure and total flow rate of the mixture gas, respectively. However, compared to gaseous precursors, this calculated flow rate is not very accurate. Since TMB in this investigation is introduced without a carrier gas directly through a MFC it will ensure very reproducible TMB mass flows and therefore reproducible boron dopant levels in the diamond coating. The accuracy of the mass flow controllers is about 1%. For reasons that have been discussed above, liquid trimethylborate was used in this thesis as the boron precursor.

![Figure 4. Illustration of 2D structure of trimethyl borate (TMB).](image)

It should be observed that using TMB as a precursor will also introduce oxygen to the gas phase. The addition of oxygen typically increases the growth rate but will also etch the non-diamond carbon components in the films [91]. Normally this means higher quality of the diamond coatings with less graphitic content.

### 3.3 Parameters setup

Apart from the precursors, many other parameters such as filament temperature, pretreatment of silicon wafer, substrate temperature, system pressure, and deposited time will influence the diamond growth process. The parameters in the presented thesis were chosen from an experimental point of view to produce well defined and nano-sized diamond coatings.

Prior to the diamond deposition, the silicon wafers with a size of 1 × 2 cm² were seeded with approximate 0.5 wt% of nanodiamond crystallites (with crystallite sizes of 4 - 5 nm, delivered by New Metals & Chemicals Corporation) in water by using a 60 min ultrasonic treatment. By using this
method, the indents on the substrate surface, which results in irregularity, are avoided as compared to seeding using scratching. Moreover, diamond slurries with a higher mass concentration or larger crystalline size of diamond and shorter ultrasonic treatment time were also investigated, but showed a lower seeding density and therefore a lower nucleation density.

Three new tungsten filaments were installed for every experiment to ensure the reproducibility of the growth process. The distance between each filament was 13 mm. The filaments were carburized using a high methane concentration (50% in hydrogen) and by a stepwise increased filament temperature up to approximate 2200°C for 30 minutes. A thin tungsten carbide layer was thereby formed to minimize tungsten evaporation and W contamination [92] of the diamond coating. Moreover, the load lock transfer chamber (see Figure 5) allows for a quick access to the substrate without breaking vacuum or filament current after carburization.

It has been reported that low pressure is beneficial for high quality nanocrystalline diamond [93]. When diamond films are deposited at a low pressure, the concentration of the reactive radicals (i.e., hydrogen radicals and CH₃ radicals) is low and the chance of collision and recombination between these radicals is thereby lower. Thus, the mean free path of these reactive radicals will increase and create an increased amount of reactive radicals impinging onto the substrate, which will create a more favorable environment for diamond nucleation. The nucleation rate will thereby increase. A total gas pressure of 5 torr was found to be optimum for the deposition of diamond films in this equipment. In addition, the reaction system is pumped out to 10⁻⁶ torr after each deposition by a turbo pump to remove any gas residue.

The filament temperature was heated to 2200°C, which was measured by a disappearing filament micro optical pyrometer (The Pyrometer Instrument Co. Inc). The distance between filament and substrate was kept constant in all experiments at about 10 mm. The typical deposition time was 4 hours and the substrate was continuously rotated at 10rpm during the deposition. These parameters were proven to give a complete coverage of the diamond film and to give an excellent uniformity [94].

One of the most important parameters in CVD is the substrate temperature. It may affect grain size [95], morphology and the direction of the crystals (texture) [96], growth rate [97] etc. Thus, different substrate temperatures (i.e., 650°C, 675°C, 700°C, 725°C and 750°C), which are recorded from the backside of the substrate and controlled by a thermocouple, were investigated. Moreover, the substrate temperature was controlled independent of the filaments, which means the substrate was heated up to approximate 600°C by the hot filaments and further heating was accomplished by a heater to obtain the desired temperature.

The content of the gas phase was also studied in the presented thesis. Two different methane flow rate and three different TMB flow rate were intro-
duced to the chamber during the deposition. More specifically, in the first series of experiments, calibrated MFCs were used to control the flow rate of H₂ at 99.5 SCCM (standard cubic centimeter) and the flow rate of CH₄ at 0.5 SCCM with varied (0.005, 0.01, 0.02 SCCM) flow rates of gaseous TMB. For the second series, with the same three kinds of TMB flow rates, the flow rate of CH₄ was set as 1 SCCM and in order to keep the same total flow rate of 100 SCCM, the flow rate of H₂ then was set as 99 SCCM. The gas path is shown in Figure 5.

![Figure 5..Scheme of the CVD equipment and gas path.](image)

### 3.4 Characterization Techniques

#### 3.4.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is a widely used technique for visualizing the morphology of nano structured surfaces. Compared to light optical microscopy, the electron beam which is emitted from an electron gun has a much shorter wavelength than visible light. This means that high resolution can be achieved. As this technique is based on the interaction between the electrons and the atoms of the sample surface, various signals can be detected to give both qualitative and quantitative information about the material. Back scattered electrons, which are incoming electrons reflected by elastic scattering, are scattered more by heavy elements than lighter elements. This is used in atomic number contrast mode, i.e., high atomic number appears brighter than low atomic number. Another common imaging mode is to detect secondary electrons, which are ejected from the surface due to inelastic scattering. The secondary electrons have a low energy, this
in turn means that they have a short escape depth. The topographical contrast is given by the angle of incidence between the incoming electron beam and the sample surface. Steep surfaces and edges tend to be brighter than flat surfaces. Two types of secondary electron detectors are commonly used, one placed in the chamber close to the projector lens and one in lens detector placed inside the electron column.

The SEM images in the presented thesis were obtained in a Zeiss 1550 with AZtec EDS, the acceleration voltage was 5kV and the working distance was normally set in between 2-6 mm. Both surface morphologies and cross-sections of the diamond films were analyzed in order to show the growth behavior and measure the film thickness.

3.4.2 Raman spectroscopy

Raman spectroscopy is a scattering spectroscopy, in which Raman effect occurs by inelastic collision between photons and molecules. More specifically, a photon from the intense monochromatic light beam will excite a molecule or compound from the ground state to a virtual energy state and stay for a short period of time. The material then relaxes to an excited state (i.e., vibrational states) while emitting another photon which can be either lower or higher in energy compared to the incoming photon. This energy difference is called the Raman shift, which is usually expressed in wavenumber (cm\(^{-1}\)) and depends on the polarizability of different compounds and structures. The Laser Raman spectroscopy is thereby an outstanding non-destructive characterization technique for identification, especially efficient for carbon thin film materials. It has been proven that the Raman spectrum is one of the most versatile signatures of synthetic diamond [98] and useful in the identification of quality of synthetic diamond (i.e., diamond-like carbons, graphitic carbons and amorphous carbons).

The Raman spectroscopy in the presented study was performed by using an in Via Raman Microscope System from Renishaw with a laser wavelength of 532 nm at room temperature. The degree of order between sp\(^2\) and sp\(^3\) phases in the diamond film was thereby estimated, in addition to the effect of boron doping.

3.4.3 Mott-Schottky plots

A Mott-Schottky plot (MSP) is well-known in the electrochemistry of semiconductors which can be used to calculate a carrier concentration (i.e., acceptor or donor) from the slope of linear part of MSP [99]. A capacitor is formed within the near surface of a semiconductor in contact with an electrolyte solution. At negative potentials of the flat band potential, \(E_{fb}\), for a p-type semiconductor (i.e., depletion conditions), the inverse of capacitance across a semiconductor-electrolyte interface is dominated by the space
charge capacitance, $C_{sc}$, as it is much smaller than double layer capacitance [100]. Moreover, the capacitance for each potential is calculated from the imaginary component of the impedance measurement with a selected frequency [101]. Thus, the boron carrier concentration in the diamond film, N, can be calculated by using the formula as follow:

$$N = \frac{2}{A^2 \varepsilon \varepsilon_0 \epsilon} \left[ \frac{d(C_{sc}^2)}{dE} \right]^{-1}$$

Eq.10

where $A$ is the surface area, $\varepsilon$ and $\varepsilon_0$ are the permittivities of diamond and free space, respectively, and $\epsilon$ is the electron charge, $d(C_{sc}^2)/(dE)$ is determined to the slope of the linear part in the MSP. In the presented thesis, the MSP is performed by an Electrochemical Workstation (CH Instruments) with a three-electrode system (Pt electrode as counter, Ag/AgCl electrode as reference) in 0.5M NaCl under 100Hz at room temperature.
4 Theoretical results

4.1 Non-doped diamond

Although the presented study is mainly focused onto the effect by the various dopants on the growth process, the non-doped scenario must be first investigated and considered as a reference. Hence, the hydrogen abstraction energies of the non-doped diamond (111), (110) and (100)-2×1 surfaces were first calculated. The results showed that different diamond surface planes have different hydrogen abstraction energies (-12, -30 and +4 kJ/mol, respectively). As compared to the adsorption energy for the growth species CH₃ (-348 kJ/mol), these abstraction energies are more positive which means less exothermic, or even positive (i.e., an endothermic reaction). Thus, the assumption of hydrogen abstraction being one of the rate-limiting steps in the diamond growth process can be applied in the present thesis.

Due to the high symmetrical diamond sp³ structure, the results of the radical Fukui function calculations were identical for each surface hydrogen atoms. This was the situation for each surface plane (e.g., see Figure 14a). This means that the reaction surface site for the hydrogen abstraction reaction can be chosen randomly for each diamond surface plane. The energy evolution for an approaching hydrogen radical to a terminated hydrogen species for the three different surface planes of diamond [(110), (111) and (100)-2×1] is shown in Figure 6a. Besides quite different values of the energy barrier for the different surface planes (5, 6 and 12 kJ/mol, respectively), the behavior of these energy curves after the energy maximum (i.e., closer to the diamond surface) do also vary. For the diamond (110) plane, the total energy will first decrease rapidly, followed by a very slow reduction and will end by a more dramatic decline to the final energy minima. However, for the (111) and (100)-2×1 planes, the energy value drops to the lowest energy, either gradually, or directly. These differences can be explained by the various extents of interaction between the hydrogen radical and the surface hydrogen adsorbate at a distance of around 1.3Å (as can be seen in Figure 7). For the (110) surface, when the approaching hydrogen radical comes close to the surface hydrogen atom, a large bond population was observed between the hydrogen radical and the terminated hydrogen, which indicates that an H–H interaction in the form of a covalent bond is starting to form. This bond population will continue to increase as the hydrogen radical approach closer to the surface hydrogen atom. Simultaneously, a decrease in bond population
for the C (surface) – H bond is taking place. Finally, a gaseous H$_2$ molecule will desorb from the surface. The C (surface) – H bond has thereby broken completely, which is strongly indicated by the resulting value of the C (surface) – H bond population (-0.04). For the approaching hydrogen radical towards the diamond (111) surface, the H – H electron population did only increase to a stabilized value of approximately the same size as the one for the C (surface) – H bond (0.55 vs. 0.45). For the situation with the (100)-2×1 surface, when the H – H distance becomes smaller, the H – H electron population was observed to somewhat increase (from zero to 0.24) and the bond population of the C (surface) – H bond remained very high (0.72). As a result, the surface-terminating hydrogen atom was still trapped at the surface. In conclusion, it is only the hydrogen radical approaching to the diamond (110) surface that will immediately result in the release of H$_2$.

The results of the calculation for desorption of H$_2$ from the surface, are shown in Figure 6b. There is no energy barrier observed for diamond (110) surface since the approaching hydrogen radical will directly induce the removal of H$_2$ from the surface. In addition, a minor energy barrier was observed to be necessary for desorption of a chemisorbed hydrogen species, in the form of an H$_2$ molecule, from the (111) and (100)-2×1 surfaces (3 and 6 kJ/mol, respectively). As compared to the energy barrier for the approaching hydrogen radical, these values are less than 50%. From these observations, it can be concluded that only the adsorption part of the hydrogen abstraction process will dominate in determining the hydrogen abstraction reaction rate, and thereafter being identical to the total growth rate (since the hydrogen abstraction process is assumed to be the rate-limiting step during diamond growth).

The Arrhenius equation can be used with the purpose to find a relation between the energy barrier and the diamond growth rate:

\[ \nu = \nu_0 \times e^{-\Delta E/RT} \]

where $\Delta E$ is the barrier energy for the adsorption process within the hydrogen abstraction, $R$ is the universal gas constant, $T$ is the temperature during the diamond growth, and $\nu_0$ is the pre-exponential factor (being assumed to be almost identical for the different diamond planes). Since it is difficult to achieve the value of $\nu_0$, the relative diamond growth rates have been calculated as:

\[ \frac{\nu_1}{\nu_2} = e^{(\Delta E_2 - \Delta E_1)/(RT)} \]

In addition, experimental growth rates for the various diamond planes have been fully investigated by Chu et al. [102]. They presented different kinetic curves for each plane using a HFCVD technique. Hence, the theoretical
modeling and simulations can be directly used to compare with, and support, the experimental results. As can be seen in Table 1, the experimental diamond growth rates at 700°C were found to have the same trend as the order of hydrogen abstraction rates from the theoretical calculations; (100) < (111) < (100)-2×1. Minor differences were though observed when comparing the relative rate (experimental vs. theoretical) in a strictly numerically manner. However, that is acceptable due to the large number of parameters that may influence the experimental growth rate. Moreover, this large similarity in numerical values and the identity in trends will strongly support the conclusion that the hydrogen abstraction process is indeed a rate-limiting step in the growth mechanism of diamond (111), (110) and (100)-2×1. Furthermore, it is clearly shown that both the theoretical methods and methodologies used in the study are adequate to use in the investigation of the effect of different dopants on diamond growth.

\[ \begin{align*} \text{(a) } & \text{Figure 6. The energy evolution curve for a) an approaching hydrogen radical to a surface terminated hydrogen species, and for b) the corresponding desorption of H}_2 \text{ molecule from the surfaces. This is demonstrated for different diamond surface planes; (110), (111) and (100)-2×1.} \end{align*} \]
Figure 7. Structural geometries at the energy minima for an approaching hydrogen radical to a surface terminating hydrogen species. This is demonstrated for the following diamond planes; (100)-2×1, (110) and (111)

Table 1. Comparison between experimental and theoretical growth rates for the non-doped diamond surface planes (110), (111) and (100)-2×1.

<table>
<thead>
<tr>
<th>diamond plane</th>
<th>growth rate (μm/h) [102]</th>
<th>relative growth rate (exp)</th>
<th>energy barrier (kJ/mol)</th>
<th>relative growth rate (theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0.24</td>
<td>1.9</td>
<td>5</td>
<td>2.4</td>
</tr>
<tr>
<td>111</td>
<td>0.19</td>
<td>1.4</td>
<td>6</td>
<td>2.0</td>
</tr>
<tr>
<td>(100)-2×1</td>
<td>0.13</td>
<td>1.0</td>
<td>12</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Relative values are related to the smallest growth rate [i.e., for (100)-2×1]

4.2 Doped diamond

4.2.1 Effect of dopants on thermodynamics

At first, the effect by different dopants, positioned within different carbon atomic layers close to the surface, on the thermodynamics (i.e., hydrogen abstraction energy) had to be evaluated to investigate the driving force for the hydrogen abstraction reaction. The results are shown in Figure 8 for the three diamond surface planes (111), (110) and (100)-2×1, as compared with the non-doped scenario. It has been shown that various dopants show different behaviors for each diamond plane. However, all of them have shown a strong effect when substitutionally positioned within the carbon layers 2 to 4. It is clear that the dopants will lead to a more exothermic abstraction energy, which means to be more preferable for the hydrogen abstraction reaction. It is thereby possible that the growth rate of diamond may increase due to these dopants incorporation within the diamond lattice. An exception is the situation with dopants within the first carbon layer, for which there is not any significant difference in result when compared to the non-doped scenario. Atomic charge, electron bond population and electron spin density calculations have been performed with the purpose to explain these observations. Because of its high degree of symmetry, the diamond (111) surface plane has been used as an example with the purpose to illustrate the analyses
procedure. The labelling, of the atoms in the diamond lattice is shown in Figure 9. The dopants are substituting the carbon atom \( \text{C}_{12}, \text{C}_{22}, \text{C}_{32}, \text{and} \text{C}_{42}, \) respectively.

![Figure 8. Surface hydrogen abstraction energy for different dopants positions within the diamond a) (111), b) (110) and c) (100)-2×1 surface planes. The non-doped scenario is demonstrated at zero number of layers.](image)

![Figure 9. Labeling of individual atoms that corresponds to the results in Table 2 and Table 3.](image)

The atomic charge of the dopants, with its surrounding atoms and the corresponding bond population values, are shown in Table 2. It is here shown that only the nitrogen dopant will have a negative atomic charge as compared to the other kinds of dopants, or substituted carbon atoms. As a consequence,
the surrounding carbon atoms are shown to have a more positive atomic charge. For other kinds of dopants, the opposite numerical values of atomic charge of the dopant and its surrounding carbon atoms, are achieved. These observations can be explained by the less electronegative of carbon (2.55), as compared to nitrogen (3.04), which gives an electron density withdrawal towards the nitrogen. On the other hand, carbon is more electronegative than boron (2.04) and phosphorous (2.19), which means that both boron and phosphorous will donating an electron density to carbon [103]. Moreover, one cannot expect any more electron transfer between sulphur and carbon due to the almost identical value of electronegativity; 2.58 (sulphur) vs. 2.55 (carbon). The more negative atomic charges of the S-binding carbon atoms are most probably a consequence of the extra valence electrons in sulphur (as compared to carbon). This extra electron density will thus be redistributed to these neighboring carbon atoms and will even lead to a reconstruction of the diamond lattice when sulphur is substitionally positioned within the upper carbon layers. For instance, when sulphur is positioned within the 1st carbon layer, the S – H bond will be tilted with a tetrahedral angle. This is the result of repulsion between the electron lone pair of sulphur and the S – H bond electron density (see Figure 10d). When sulphur is positioned within the 2nd or 3rd carbon layer, one of the S – C bonds will break (see Figure 10) due to positioning of the extra valence electrons in antibonding molecule orbital states.

Moreover, since the phosphorous, nitrogen, and boron dopants will induce an unpaired electron (i.e., spin) into the diamond system, the distribution of this spin in the diamond system has been investigated by performing spin density calculations (the results are shown in Figure 10). With phosphorous and nitrogen positioned within the 2nd, 3rd and 4th carbon layer, the spin density was distributed within the C (surface) – H bonds and more focused on the carbon atoms (i.e., without changing the atomic charges of the surface hydrogen atoms). Hence, these two dopants will donate the extra electron to some surface carbon atoms. These spin densities will weaken the C (surface) – H bonds, which can be shown by calculating the C – H electron bond populations (demonstrated in Table 3). As a consequence, the more exothermic hydrogen abstraction energy is achieved, and will lead to an improve abstraction process with phosphorous and nitrogen incorporated into the diamond lattice. Moreover, with a decreased intensity of this spin density around the C (surface) – H bond, for the situations with these two dopants positioned further down into the diamond lattice, the C (surface) – H bond population was found to increase when moving the dopant from carbon layer 2 to 4. These observations correlate well with the less exothermic hydrogen abstraction energy when going from the dopant in layer 2, to the dopant in layer 4. The underlying reason is most probably that it is more easy to weaken the C (surface) – H bond when the extra valence electron in phosphorous, or nitrogen, in the 2nd layer is closer to the surface. In addition to
these effects by phosphorous and nitrogen on the electron structure, the larger radii of the phosphorous atom will also lead to a more easily donation of the extra valence electron to the surface (as compared to nitrogen). As a result, when phosphorous is positioned within the upper carbon layers in the diamond lattice, there is a more pronounced distribution of spin density to the surface (as compared to the nitrogen dopant). These results are demonstrated in Figure 10, where the surface behaviors (i.e., the distribution and intensity of the spin density) are identical for phosphorous (series a) and nitrogen (series b), but with different isovalues (0.01 vs. 0.004). In addition to the hydrogen abstraction energy, the corresponding bond population of C (surface) – H, was also found to be more influenced by phosphorous doping.

Table 2. Results from the Atomic Charge Calculations for different dopants and its surrounding atoms in a diamond (111) surface plane. The non-doped situation is demonstrated with a zero doping layer. A is the dopant atom.

<table>
<thead>
<tr>
<th>Doping layer</th>
<th>Atom</th>
<th>Mulliken atomic charge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>0</td>
<td>H₂</td>
<td>+0.23</td>
</tr>
<tr>
<td></td>
<td>C₁₂</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>C₂₂</td>
<td>+0.02</td>
</tr>
<tr>
<td>1</td>
<td>H₂</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>+0.73</td>
</tr>
<tr>
<td></td>
<td>C₂₁</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>C₂₂</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>C₁₃</td>
<td>-0.25</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>+0.23</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>+1.51</td>
</tr>
<tr>
<td></td>
<td>C₁₂</td>
<td>-0.59</td>
</tr>
<tr>
<td></td>
<td>C₁₃</td>
<td>-0.59</td>
</tr>
<tr>
<td></td>
<td>C₃₂</td>
<td>-0.28</td>
</tr>
<tr>
<td></td>
<td>C₁₁</td>
<td>-0.27</td>
</tr>
<tr>
<td>3</td>
<td>H₂</td>
<td>+0.23</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>+1.50</td>
</tr>
<tr>
<td></td>
<td>C₂₂</td>
<td>-0.25</td>
</tr>
<tr>
<td></td>
<td>C₄₁</td>
<td>-0.30</td>
</tr>
<tr>
<td></td>
<td>C₄₂</td>
<td>-0.30</td>
</tr>
<tr>
<td></td>
<td>C₁₂</td>
<td>-0.28</td>
</tr>
<tr>
<td>4</td>
<td>H₂</td>
<td>+0.23</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>+1.54</td>
</tr>
<tr>
<td></td>
<td>C₃₁</td>
<td>-0.30</td>
</tr>
<tr>
<td></td>
<td>C₃₂</td>
<td>-0.31</td>
</tr>
<tr>
<td></td>
<td>C₃₃</td>
<td>-0.31</td>
</tr>
<tr>
<td></td>
<td>C₁₂</td>
<td>-0.27</td>
</tr>
</tbody>
</table>
Table 3. Results from the Bond Population Analysis for the C – Dopant bonds and C (surface) – H bonds. The non-doped situation is demonstrated with a zero doping layer. A is the dopant atom.

<table>
<thead>
<tr>
<th>Doping layer</th>
<th>Bond</th>
<th>Electron bond population</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>P</td>
</tr>
<tr>
<td>0</td>
<td>C\textsubscript{12}-H\textsubscript{2}</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{12}-C\textsubscript{22}</td>
<td>0.81</td>
</tr>
<tr>
<td>1</td>
<td>C\textsubscript{13}-H\textsubscript{3}</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>A-H\textsubscript{2}</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{21}-A</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>C\textsubscript{22}-A</td>
<td>0.68</td>
</tr>
<tr>
<td>2</td>
<td>C\textsubscript{12}-H\textsubscript{2}</td>
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<tr>
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</tr>
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<tr>
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<td>0.82</td>
</tr>
<tr>
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<td>C\textsubscript{32}-A</td>
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<tr>
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Figure 10. Calculated electron spin densities for the situation with a) phosphorus, b) nitrogen, c) boron and d) sulfur positioned in the A) first, B) second, C) third and D) forth atomic carbon layer, respectively.

With boron positioned within the 2nd, 3rd or 4th carbon layer, the spin density was only localized to three C – B bonds (as shown in Figure 10c). Thus, related to the C – B bond population, there are three almost identical values (0.78 – 0.81) and one larger value (0.85, 0.84, and 0.84 for boron doping within the 2nd to 4th carbon layer, respectively) (as shown in Table 3). This observation is opposite to the nitrogen doping scenario, where there is three identical values (0.64) and one that is smaller (0.59, 0.56, and 0.55 for nitrogen doping within the 2nd to 4th carbon layer, respectively) (see Figure 10b and Table 3). For the phosphorous doping scenario, no spin density distribution was observed within the C – P bonds and thereby, the four C – P bond populations were equivalent.

For the situation with boron doping, it has been shown that the atomic charges of the surface hydrogen atoms that are close to the boron dopant will decrease, which means a lowering of the withdrawal capability of the surface carbon atoms. [41]. Thus, for the situation with boron positioned within the 2nd to 4th carbon layers, the C (surface) – H bond population will decrease as compared to the non-doped situation. (see Figure 10c). It is though believed that the spin density localized onto the C – B bonds will inhibit this decrease. Since the doping of boron in lower positioned carbon layers shows a smaller effect on the surface, the effect of lowering the electron withdrawal effect
from the hydrogen atom towards the boron dopant will become less accentuated (i.e., an increase in atomic charge of surface hydrogen atoms). Thus, the bond population of the C (surface) – H bonds is not expected to decrease appreciably for boron positioned in the lower carbon layers. However, the effect of spin density, which is only localized around the atoms, will also become less pronounced when positioning boron within lower carbon layers. Thus, it will not be possible to inhibit the decrease of the C (surface) – H bond population. As a result, the bond population will decrease more when boron is positioned within the 3rd carbon layer (0.87 vs. 0.88, as compared to boron doping in 2nd carbon layer) and decrease to the same value when boron is positioned within the 4th carbon layer (0.88). These observations strongly support the hydrogen abstraction energy curve for boron doping within the diamond (111) plane, where the abstraction energy value is almost equivalent for boron doping within the 2nd and 3rd carbon layer, and becomes less exothermic with boron doping within the 4th carbon layer.

Although the hydrogen abstraction energy curve will continuously decrease (i.e., towards more exothermic values), the situation for sulphur doping is more complex than for any of the other dopants. As shown in Table 2, the upper diamond structure will be quite different when substituting a carbon atom with sulphur for the carbon layers 1, 2, and 3, respectively. When sulphur is positioned into the 1st carbon layer, the S – H bond will be tilted as a result of repulsion between the extra electron pair in sulphur and the S – H bond electrons. However, the S – H bond population is extremely low (0.06), which means that it is very easy to break this bond. Therefore, the corresponding abstraction energy of this H atom is very negative (-247 kJ/mol). Furthermore, when sulphur is substitutionally positioned within the 2nd carbon layer, it has been found that the extra electron pair in sulphur will split up. One electron stays at the sulphur atom whilst the other moves over to the binding C32 atom further down in the lattice. As a consequence, sulphur will bind to three surface carbon atoms and still have a stable electron pair. The C32 – S bond will thus break which leads to the formation of an electron pair on C32 as well. The repulsions between these resulting electron pairs on C32 and sulphur, in addition to the fact that the sulphur atomic radius is larger than for carbon, will induce a relaxation of sulphur atom towards the upper surface layer. The calculations of the atomic charges have shown results that strongly support these observations, where the extra electron density will redistribute from the sulphur atom to the neighboring carbon atoms. The closest C (surface) – H bonds will thereby be weakened with a resulting electron bond population value of 0.81. The hydrogen abstraction energy will thus become very negative (-173 kJ/mol). When sulphur is substitutionally positioned within the 3rd carbon layer, there will also here be structural constraints in the lattice which is identical to the situation with sulphur positioned in the 2nd carbon layer. However, there is a high level of electron spin density at the sulphur binding C22 atom. This is an indication of the fact that
there is no formation of an electron pair at this specific C_{22} site as a result of the C_{22} – S bond breakage. Thus, unlike sulphur within carbon layer 2, where the closest C (surface) – H bonds have an electron bond population value of 0.81, these bonds will be strengthened (with a bond population of 0.92). The reason is the same as for the boron doping scenario (i.e., the spin density localized to the boron atom will have the effect to enhance the bond population of C (surface) – H bonds closest to the dopant). Still, the hydrogen abstraction energy will decrease (i.e., with a more exothermic reaction) as compared to the non-doped situation (-192 vs. -12 kJ/mol). The reason why these very exothermic hydrogen abstraction values are not shown in Figure 8a is that these abstraction processes only exist for the hydrogen directly linked, or being closest, to the sulphur atom. Since the doping level is very low in practice, the surface coverage of these especially binding hydrogen atoms, is also very low. Thus, the hydrogen abstraction energy from the next-nearest surface hydrogen atom (i.e., C (surface) – H) to the dopant has to be investigated. The electron bond population within these C (surface) – H bonds is though almost as large as for intrinsic diamond, which means that the hydrogen abstraction energy is also almost the same for sulphur positioned within the 1\textsuperscript{st} or 2\textsuperscript{nd} carbon layers. Despite the increase in bond population for the next-nearest C (surface) – H bonds (0.90), with sulphur doping within the 3\textsuperscript{rd} carbon layer, the more exothermic hydrogen abstraction energy is observed. More interesting results exists for the situation with sulphur within carbon layer 4, for which there isn’t any size effect (which for the other sulphur doping situations caused more or less severe structural changes). Hence, the sulphur dopant seems to be trapped into the 4\textsuperscript{th} carbon layer. The donation of the two extra electrons will thereby be different. The spin density calculations show that there is a distribution of electron density predominantly at the S – C bonds. In addition, there is also a minor distribution of spin density at the surface, which most probably causes the decrease in bond population for the C (surface) – H bonds, and with a corresponding lowering of the hydrogen abstraction energies.

An exception to these situations is the position of dopants within the 1\textsuperscript{st} carbon layer, for which phosphorous, nitrogen, and boron preferred to bind to only three neighbouring carbon atoms (i.e., 3 C – dopant bonds). The extra electron did thereby form a lone pair with the electron that otherwise would have been expected to form a dopant – H bond. Hence, neither electron spin densities, nor changes in hydrogen atomic charges (i.e., H\textsubscript{1} in Figure 9), as compared to the non-doped situation, was thereby observed. As a consequence, there is almost no difference in hydrogen abstraction energy when positioning these dopants within the 1\textsuperscript{st} carbon layer in diamond (111).

In addition to the effect by doping further down into the diamond lattice, it is also important to investigate the effect by doping on the lateral distance to the dopant site. Since phosphorous, nitrogen, and boron doping within the 2\textsuperscript{nd} carbon layer, and sulphur within the 4\textsuperscript{th} carbon layer, resulted in the most
exothermic hydrogen abstraction energies, they are here also chosen as models for the lateral doping effects. The results for these different dopants show almost the same behaviors. It is found that the abstraction energy will increase (i.e., a less exothermic reaction) when the distance between the dopant and the hydrogen abstraction site becomes longer. This is quite natural since the influence by the dopant must decrease. However, there are though minor differences for the sulphur dopant situations as compared to other dopant types (i.e., since there is a steep ascent between position 1 and 2 (labelled in Figure 12) for phosphorous, nitrogen, and boron doping, but not for sulphur doping). A more detailed analysis for the phosphorous and sulphur scenarios has therefore been performed. For the situation with phosphorous doping within the 2\textsuperscript{nd} carbon layer, the spin density is predominantly localized around the dopant (as shown in Figure 11). Hence, the phosphorous dopant does only show a very local effect, which will explain the sharp ascent in abstraction energy when laterally moving towards hydrogen sites further away from the phosphorous dopant. This ascent in abstraction energy becomes though quite small between abstraction site 2 and 6 (labelled in Figure 12) since there is continuously smaller and smaller spin densities when moving further away from the dopant. There is a similar situation for the sulphur doping within the 4\textsuperscript{th} carbon layer, but for this situation the spin density is more spread out around the dopant. The abstraction energy values for the sulphur doping do therefore become less negative in a continuous and non-abrupt way (see Figure 12).

Similar investigations have also been carried out for phosphorous positioned within the 3\textsuperscript{rd} carbon layer. The hydrogen abstraction energy thereby increased from -166 to -121 kJ/mol, and then levelled out to -91 kJ/mol when laterally moving towards hydrogen sites further away from the phosphorous dopant. Thus, the local effect is though not as obvious as for the situation with phosphorous doping within the 2\textsuperscript{nd} carbon layer. However, as can be seen in the series c of Figure 10, the spin density is quite localized around the boron dopant which means that the effect by boron is quite local. Hence, the local effect is still obvious for the situation with boron doping within the 3\textsuperscript{rd} carbon layer. This is supported by the results of the hydrogen abstraction energy calculations, which show an increase from -142 to 35 kJ/mol when laterally moving hydrogen sites further away from the boron dopant within the 3\textsuperscript{rd} carbon layer.
Figure 11. Surface hydrogen abstraction energy for various dopants within different lateral positions relative the hydrogen abstraction site (which are shown in Figure 12).

Figure 12. The isosurface of spin densities (ontop view) for a) phosphorous positioned in the 2\textsuperscript{nd} layer, and b) sulphur positioned in the 4\textsuperscript{th} layer. The pink ball and the yellow ball represent a phosphorous atom and sulphur atom, respectively. Their substitutional positions in the lattice are represented at the left corner of the figures. The labeling numbers are the different hydrogen abstraction sites.
4.2.2 Effect of dopants on surface reactivities

The fact that these dopants have an effect on the hydrogen abstraction reaction, when they are substitutionally positioned within the carbon layers in the diamond lattice, indicate that the surface reactivity also will change. In order to further analyze the effect on surface reactivities, the Fukui function $f^{(0)}$ was calculated with the purpose to localize the most reactive site for a hydrogen radical attack. The results of 3D Fukui function calculations for radical susceptibility are shown in Figure 13. There is a major effect on $f^{(0)}$ when using phosphorous doping, for which the most reactive area was observed to be localized at the surface (especially the situation when positioning phosphorous within the 2$^{nd}$ carbon layer). As compared with the non-doped diamond situation, the surface showed a somewhat larger degree of reactivity when positioning phosphorous within the 2$^{nd}$, 3$^{rd}$, and 4$^{th}$ carbon layer, respectively. However, no specific increase in surface reactivity was observed for phosphorous positioned within the 1$^{st}$ carbon layer. These results do strongly correlate with the hydrogen abstraction energies. More specifically, the hydrogen abstraction reaction is most exothermic, in addition to that the surface sites are most susceptible for a radical attack, for the situation with phosphorous in the 2$^{nd}$ carbon layer. When the hydrogen abstraction reaction becomes less exothermic, for the situation with positioned dopants further down into the lattice, also the surface reactivity will decrease.

When boron is positioned within the 1$^{st}$ carbon layer, a very reactive surface is introduced. However, this reactive site is quite localized to the boron dopant, whilst the reactivity of the other surface sites are kept the same as for a non-doped situation. This means that the effect of boron within the 1$^{st}$ carbon layer on the surface is quite limited. Thus, the corresponding surface properties (i.e., C (surface) – H bond population and hydrogen abstraction energy) are almost identical to the non-doped diamond situation. Moreover, a local effect has also been observed when positioning boron further down into the lattice. Hence, the surface reactivity dramatically drops, and becomes even smaller compared to the non-doped situation. Although the hydrogen abstraction energy is more exothermic when positioning boron within the 3$^{rd}$ carbon layer, as compared with the 2$^{nd}$ carbon layer, it does not show more susceptible for a hydrogen radical attack. Actually, an increase in surface reactivity was observed when substitutionally positioning boron within the 2$^{nd}$ carbon layer. This observation is relative to the electron redistribution from the boron atom to the surface carbon atom (i.e., C$_{12}$ in the Figure 9) and lead to more negative atomic charge (-0.38) of these surface carbon atoms [as compared to the non-doped scenario (-0.24)]. This electron redistribution to the surface carbon atoms was only observed for boron positioning within the 2$^{nd}$ carbon layer. The surface reactivity was almost identical to the non-doped scenario when boron was positioned within lower carbon layers.
The effect by substitutionally doping with sulphur is quite different. For all different positions of the sulphur dopant, the sulphur atom was observed to be more reactive than any other atoms. A quite reactive, and localized, site around the sulphur dopant was thereby observed. An exception is though the situation with sulphur positioned within the 4th carbon layer, for which $f^{(0)}$ was observed to also be located in parallel with the surface and ontop of the surface hydrogen atoms. As a consequence, it is only the doping of sulphur in the 4th carbon layer that renders a more reactive surface. These results are interesting, because they are again strongly correlated to the calculated values of the hydrogen abstraction energy, which was found to be most negative for sulphur incorporated within the 4th carbon layer.
Since it was not clear in which form the dopant will improve the diamond growth rate, also adsorbed dopant-containing species had to be investigated. For instance, nitrogen can be attached to the surface in the form of either a radical NH group or an NH$_2$ group. It was found that the non-paired electron in the radical NH group will stay locally at the NH entity, and will thereby not show any tendency to weaken the C (surface) – H bond. The Fukui function calculations have also shown that the surface reactivity is localized at the NH adsorbate (see Figure 14d). Due to this reason, the energy barrier for hydrogen abstraction process from C (surface) – H bond is expected to be
very similar as for the non-doped diamond surface, and these calculations have hence not been included in the present study. However, when nitrogen is chemisorbed in the form of NH$_2$ onto the diamond surface, the reactivity of the surface hydrogen in the vicinity to the hydrogen atoms within the NH$_2$ group is enhanced, whilst the one closest to the nitrogen atom will decrease in reactivity (see Figure 14c). Moreover, there is a major effect by the substitutionally positioned nitrogen dopant within the 2$^{nd}$ carbon layer on the radical susceptibility. Although this effect is localized around the nitrogen dopant, the surface reactivity is strongly reinforced as compared to the non-doped situation (see Figure 14b).

Based on the radical Fukui function calculations, the most reactive surface hydrogen terminator was chosen and allowed to take part in a hydrogen abstraction process for which the kinetics were highlighted. For the situation with phosphorous, or nitrogen, substitutionally positioned within the carbon layers, the surface hydrogen atom to which the approaching hydrogen radical did attack was chosen as the one closest to the phosphorous, or nitrogen, atom. The reason is that the most reactive site was located close to the dopant (as shown in Figure 12a and Figure 14b), and for which the hydrogen abstraction energy was most exothermic. As is the situation for boron,
positioned within the 2\textsuperscript{nd}, 3\textsuperscript{rd}, and 4\textsuperscript{th} carbon layer, and for sulphur positioned within the 4\textsuperscript{th} carbon layer, the most reactive, and thereby chosen, surface hydrogen atom was the one closest to the dopant atom. For the situation with sulphur doping within other carbon layers, it was difficult to choose an optimal surface reaction site for the approach of a gaseous hydrogen atom due to the quite localized reactive site. The most reactive hydrogen termination site was therefore chosen where the lowest C (surface) – H bond population is. The electron bond population has been shown as a good tool in the search for the most reactive site since it generally measures the level of covalency in a bond.

4.2.3 Effect of dopants on kinetics

In order to investigate the kinetics of the hydrogen abstraction process and thereafter to compare the growth rate between the non-doped and doped situation, the energy barriers for a free hydrogen radical attacking the surface had to be evaluated. These calculations were compared with the experimental observations obtained from a CVD process. The values of hydrogen abstraction energy barrier for the different diamond surface planes, and for different dopants with various kinds of doping positions are shown in Table 4. The most interesting results were obtained for some doping scenarios (i.e., phosphorous positioned below the 2\textsuperscript{nd} carbon layer, nitrogen or boron positioned within the 2\textsuperscript{nd} carbon layer, and sulphur positioned within the 4\textsuperscript{th} carbon layer) for which there are no energy barriers detected for the approaching hydrogen radical to the surface. For these situations, when analyzing the interaction between the incoming hydrogen and the surface hydrogen terminating atom, the electron density calculations have shown that the C (surface) – H bond population will decrease [e.g., from 0.61 to 0.53 for phosphorous positioned within the 2\textsuperscript{nd} carbon layer of diamond (111)], whilst the electron population between the incoming hydrogen radical and the surface hydrogen atom will increase. That indicates an electron orbital overlap between the approaching hydrogen radical and the surface hydrogen atom, with a resulting partial electron transfer from the surface hydrogen atom to the approaching hydrogen radical. Hence, these specific dopants will induce a strong interaction between the surface and the incoming hydrogen species. These results are strongly correlated with the observations of hydrogen abstraction energy, C (surface) – H bond population and surface reactivity, where the hydrogen abstraction energy is the most exothermic, the bond population is the lowest and the surface reactivity is the highest for these specific dopant positions.

The lateral effect of the dopant has also been studied by calculating the energy barrier, and by choosing other attack sites (i.e. further away from the dopant) for the incoming hydrogen radical. The energy barriers were still observed to be zero for most of the attack sites with phosphorous positioned
within the 2nd carbon layer. However, it was only when the attack site was closest to the phosphorous dopant, when a hydrogen molecule was automatically formed. That means that there is an especially strong interaction for that particular attack site.

On the contrary a more global effect was observed with sulphur positioned in the 4th carbon layer. When laterally moving the attack site for the hydrogen radical, with respect to the sulphur dopant position, there was no change in hydrogen abstraction process. Although the C (surface) – H bond population will increase when laterally moving the hydrogen abstraction site further away from the sulphur dopant, there is an identical degree of interaction between the surface and the incoming hydrogen radical. For example, when approaching the hydrogen radical to the surface hydrogen atom at position 1 (labelled in Figure 12b), the C (surface) – H bond population was observed to decrease from 0.74 (without approaching hydrogen radical) to 0.68. For the hydrogen radical attacking site at the position 3, this population was observed to decrease from 0.84 (without approaching hydrogen radical) to 0.79. Moreover, the bond population was observed to decrease from 0.86 (without approaching hydrogen radical) to 0.81 for an hydrogen radical attacking site at position 5. The very similar reduction in bond population values (approximate 0.06) indicate a global effect by sulphur doping within the 4th carbon layer.

Due to pronounced localized effect by the boron doping, it shows that the energy barrier for the hydrogen abstraction process will increase when laterally moving the attack site from the dopant position. For example, with boron substitutionally positioned within the 2nd carbon layer, the energy barrier will increase from 0 to 3.8, and level out to 6.6 kJ/mol.

Moreover, the electron bond populations at the energy maximum have also been calculated for the approaching hydrogen radical to the surface. It was found that the numerical value of the energy barrier is correlated to the value of the increased bond population of the C (surface) – H bond at this energy maximum. For the situation with phosphorous positioned within the 1st carbon layer, and with sulphur positioned within the 2nd or 3rd carbon layer, the value of the transition state C (surface) – H bond population did markedly increase from 0.90 (without approaching hydrogen radical) to 0.95, 0.81 (without approaching hydrogen radical) to 0.90, and 0.90 (without approaching hydrogen radical) to 0.96, respectively. It is to be compared with the situation for non-doped diamond [from 0.89 (without approaching hydrogen radical) to 0.91]. Hence, these doping situations will have a profound influence on the transition state for the incoming hydrogen radical. As a matter of fact, the C (surface) – H bond populations will increase much more as compared to the non-doped scenario, to be compared to the non-doped situations, this increase is almost twice as large as for the energy barriers of the hydrogen abstraction process (see Table 4 for these special doping situations).
The bond population of the C (surface) – H bond at the transition state will also increase for both the situation with boron positioned within the 1st carbon layer [from 0.91 (without approaching hydrogen radical) to 0.94], and with boron within the 3rd carbon layer [0.87 (without approaching hydrogen radical) to 0.90]. Since these changes in C (surface) – H bond populations are just a little bit more improved as compared to the non-doped scenario, the values of the energy barrier for the hydrogen abstraction process are also a bit larger as compared to the non-doped scenario. These observations indicate that the energy barrier for the hydrogen abstraction process will appear when the bond population of the C (surface) – H bond is increased during the process of an approaching hydrogen radical. Hence, the value of this energy barrier depends on the degree of the increasing C (surface) – H bond population.

Based on the study of the non-doped situation (as presented in Section 4.1 Non-doped diamond), the experimental effect by the dopants on the diamond growth rate can be estimated on the basis of the kinetic study. Under the assumption that the hydrogen abstraction process is a rate-limiting growth step, the different energy barrier values for the hydrogen abstraction reaction can be used in calculating the ratios of diamond growth rate for various doping situations and for different diamond surface planes (see Eq.12). As a result, there is a remarkable increase in growth rate when introducing hydrogen within the 2nd carbon layer, which has been calculated with a factor of 3.7 (for diamond (100)-2×1 plane at 1073 K), as compared with the non-doped scenario. An almost identical ratio enhancement of growth rate (i.e., with a maximum value of 3.5) was also found in an experiment within a MWPA-CVD reaction chamber at 1073 K. Although there is no experimental work that did consider the effect of other dopants on the specific diamond planes, the experimentally obtained increased in diamond growth rate for phosphorous doping can be explained by the zero-level energy barrier. This excellent correspondence between theory and experiments confirm that it is most probably the phosphorous dopant, incorporated in the lattice, that is responsible for the growth rate enhancement. However, sulphur and boron doping will lead to anomalous changes in the diamond growth rate (i.e., either increase or decrease), depending on the position of these two dopants in the lattice. More specifically, the growth rate will increase when sulphur is present in the 4th carbon layer, or boron in the 2nd carbon layer, since there is no energy barrier for these situations. For other doping positions, there are much larger energy barriers as compare to the non-doped scenario. Thus, there will be a decrease in diamond growth rate. This phenomenon is also strongly supported by the experimental observations, which indicate both an increased and a decreased effect on the diamond growth rate by performing a sulphur, or boron doping, in the lattice (see Section 1.3.2 Boron doping and Section 1.3.4 Sulphur doping.)
Table 4. Effect of various dopants when substitutionally positioned within different carbon layers, or chemisorbed as a XH$_2$ group onto the surface, on the energy barrier (kJ/mol) for the hydrogen abstraction process onto the diamond (111), (110) and (100)-2×1 surface plane, respectively.

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5 Experimental results

5.1 Morphology

*Figure 16* shows SEM micrographs of boron doped diamond films as a function of the TMB and CH₄ flow rate at a deposition temperature of 675 °C. A typical feature in all pictures is lamellar shaped twin grains, probably a mixture of a (110) and a (111) texture [33]. Similar results have previously been obtained by others [104]. Except for the lowest TMB concentrations the morphology does not change much. At the lowest concentrations the diamond grains seem to be etched to some degree, see *Figure 16 a₁* and a₂. Such an etching effect could have been caused by the oxygen in TMB. It is also known that (110) textures are favored by TMB [33].

Moreover, the morphology of the diamond films, with same gas composition but different temperature, is almost identical. That means the morphology of the diamond film within the temperature range (i.e., 625°C to 750 °C) of this study did not change much. An example of two experimental series showing the morphology as a function of increasing temperature, with 0.5 SCCM CH₄ and 0.01 SCCM TMB flow rate, is shown in *Figure 15*. As can be seen, the morphology and grain size did not change much in this temperature interval.

*Figure 15*. SEM images of the boron doped films deposited with CH₄ flow rate of 0.5 SCCM and TMB flow rate of 0.01 SCCM at a) 650 °C, b) 675 °C, c) 700 °C, d) 725 °C, e) 750 °C, respectively.
5.2 Raman spectroscopy

The Raman spectra for the two series of samples discussed in Section 5.1 Morphology (i.e., the diamond films deposited at 675 °C) are shown in Figure 17. The first order Raman phonon peak of diamond (sp³) at 1332 cm⁻¹ is present in all samples. However, when the TMB flow rate increases, this peak is shifted a little to a lower wavenumber (e.g., to 1327 cm⁻¹ using 1 SCCM CH₄ and when the flow rate of TMB was increased from 0.005 to 0.02 SCCM). It has been explained by Prawr and Nemanich by the Fano-type interference between the discrete zone-centre and the continuum of electronic state induced by boron doping [105]. Moreover, the existence of sp²-hybridized carbon was also shown in the film by the G-peak (around

Figure 16. SEM images of the B-doped films deposited at 675 °C with CH₄ flow rate of (a) 0.5 SCCM and (b) 1 SCCM and different TMB flow rate 1) 0.005 SCCM, 2) 0.01 SCCM and 3) 0.02 SCCM.
1530 cm\(^{-1}\)). This G-peak becomes weaker in the sample of 0.5 SCCM CH\(_4\) flow rate as compared to the sample of 1 SCCM, and in the sample of higher TMB flow rate. This means the gas phase with 0.5 SCCM CH\(_4\) flow rate and higher TMB flow rate produced better quality (i.e., less sp\(^2\) carbon species) diamond films.

The other two peaks around 500 cm\(^{-1}\) and 1230 cm\(^{-1}\) are consistent with the two maxima of phonon density of states (PDOS) for diamond that is doped with boron [105] and the intensity will thereby increase with increasing TMB flow rate. Moreover, it has been reported that the wavenumber of the Lorentzian fitting component to the 500 cm\(^{-1}\) peak can be used to deduce the boron concentration in the diamond films using the equation below [106]:

\[
[B] = 8.44 \times 10^{30} \exp (-0.048W) \quad \text{Eq.13}
\]

where B is the boron doping level in the film, W is the wavenumber of the Lorentzian fitting to the 500 cm\(^{-1}\) peak. Since some of the diamond films are quite thin (i.e., 2 \(\mu\)m), the silicon peak (at 521 cm\(^{-1}\)) may also be detected and overlap with the 500 cm\(^{-1}\) peak (see Figure 17). However for thicker samples (i.e., 4 \(\mu\)m), where the silicon peak is not present, the method can be used. One example is the sample deposited with 1 SCCM CH\(_4\) and 0.02 SCCM TMB flow rate (T=675 °C), where the doping level in the diamond coating was calculated to 4.05\(\times\)10\(^{20}\) atom/cm\(^3\). This result was close to what Tsigkourakos et. al. [107] measured under similar conditions using SIMS (secondary ion mass spectrometry) 6\(\times\)10\(^{20}\) atom/cm\(^3\). However, in the following Mott-Schottky Plots was used to calculate the boron carrier concentration in the diamond films. One reason for not using the Raman method entirely in this thesis was because the method can only handle moderate high doping levels.
5.3 Boron carrier concentration

The results of the boron carrier concentration which are calculated from MSP from Eq.10 are shown in Table 5 as a function of the TMB flow rate and the substrate temperature. These carrier concentrations closely follow the TMB gas phase concentration, i.e. when the concentration of TMB is doubled also the dopant level is roughly doubled. However, as a function of temperature, the dopant level will first decrease with increasing temperature up to 675 °C, then the dopant level again increases and level off when further increasing the temperature. This trend is totally opposite to the growth...
rate but the change in the trend coincides with the change of deposition mechanism control at 675 °C.

Another interesting observation is that the boron carrier concentration in the diamond films mainly depends on the mass flow rate of TMB (i.e., the total mass flow introduced into the chamber) but is almost independent on the mass flow of CH₄ at the same deposition temperature.

Moreover, as compared to the boron doping level obtained from the Raman spectra (see Section 5.2 Raman spectroscopy), the result of boron carrier concentration from MSP is 20 times larger. This big difference is relative to the real surface area of the diamond films. The characterization of Raman spectroscopy is independent to the surface area, while the MSP is quite sensitive to the surface area as shown in Eq.10 where A is the real surface area of the diamond film. The results of the boron carrier concentration are calculated under the assumption of a totally flat ideal surface. Due to the high roughness of the diamond films, as can be seen in Figure 16, and that the carrier concentration is inversely proportional to the square of the area when using the MSP, the boron carrier concentration can only approximately be used to compare with results from other characterizations techniques such as Raman spectroscopy and SIMS. However, assuming that the morphology of the diamond films did not change significantly with temperature, the relative values of MSP can still be used.

Table 5. The boron carrier concentration with various gas composition and substrate temperature

<table>
<thead>
<tr>
<th>CH₄ (SCCM)</th>
<th>TMB (SCCM)</th>
<th>Boron carrier concentration with various substrate temperature (10²¹ atom/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>625°C</td>
</tr>
<tr>
<td>0.5</td>
<td>0.005</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>4.69</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>10.71</td>
</tr>
<tr>
<td>1</td>
<td>0.005</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>4.71</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>10.73</td>
</tr>
</tbody>
</table>

5.4 Growth rate

From the cross-sectional micrographs of the diamond films, the growth rate can be obtained though the film thickness. The results for both experimental series are shown in Table 6. The results from one more experimental series with 2 SCCM CH₄ and 0.01 SCCM TMB flow rate as a function of temperature is also shown there. It can be seen that the growth rate increased rapidly, for example from 0.54 μm/h to 0.76 μm/h when increasing the temperature
from 625 to 675 °C using 0.5 SCCM CH$_4$ and 0.005 SCCM TMB flow rate was introduced into the chamber. When further increasing the temperature the growth rate decreased slightly to 0.63 μm/h. These two regions coincide with two types of control of the CVD process which will be discussed more in Section 5.5 Apparent activation energy. Moreover, the growth rate was almost twice as large when the CH$_4$ flow rate was doubled. On the other hand, different TMB flow rates affected the growth rate much less. When the TMB flow rate was increased, the growth rate stayed almost constant, see Table 5. This will also be discussed more in Section 5.6 Reaction order.

Table 6. The growth rate with various gas composition and substrate temperature.

<table>
<thead>
<tr>
<th>CH$_4$ (SCCM)</th>
<th>TMB (SCCM)</th>
<th>Growth rates with various substrate temperatures (μm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>625°C</td>
</tr>
<tr>
<td>0.5</td>
<td>0.005</td>
<td>0.54</td>
</tr>
<tr>
<td>0.5</td>
<td>0.01</td>
<td>0.56</td>
</tr>
<tr>
<td>0.5</td>
<td>0.02</td>
<td>0.59</td>
</tr>
<tr>
<td>1</td>
<td>0.005</td>
<td>1.25</td>
</tr>
<tr>
<td>1</td>
<td>0.01</td>
<td>1.29</td>
</tr>
<tr>
<td>1</td>
<td>0.02</td>
<td>1.32</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>2.14</td>
</tr>
</tbody>
</table>

5.5 Apparent activation energy

The apparent activation energy of a deposition process under surface kinetics control can be calculated from the Arrhenius equation below:

$$G = A e^{\frac{E_a}{kT}}$$  \hspace{1cm} Eq.14

where \(G\) is the thickness growth rate, \(A\) is a frequency factor, \(E_a\) is the activation energy, \(R\) is the gas constant, and \(T\) is the substrate temperature (in K). With the growth rate data observed in Fel! Hittar inte referenskälla., a linearized plot of the Arrhenius equation can be obtained as shown in Figure 18. Typically such plots are used to distinguish between different types of control of the CVD process. As mentioned in Section 5.4 Growth rate, an exponential increase in deposition rate with increasing temperature indicates that the diamond CVD process is kinetically controlled and mass transport controlled when the growth rate levels off or decreases. Moreover, in the kinetically controlled region the apparent activation energy (\(E_a\)) can be calculated from the slope.

The surface kinetics control mainly shows that the deposition process is determined by the surface reactions and surface diffusion including nuclea-
tion and in some cases by adsorption or desorption. The reactants can rapidly diffuse through the boundary layer and the amount of reactants reaching the surface is independent of the temperature but larger than the rate consumed by the surface reactions.

Figure 18. Arrhenius plot of the logarithm of the thickness growth rate vs. the reciprocal of the substrate temperature. The inset value is the activation energy. Plotted are the respective TMB flow rate: 0.005 SCCM (black squares), 0.01 SCCM (red circles) and 0.02 SCCM (blue triangles).

The decreasing boron carrier concentration when increasing the deposition temperature in the low temperature region (Table 5) indicates that the diffusion of TMB may be transport limited at lower temperatures than 675 °C. This cannot be seen in the Arrhenius plots since TMB does not affect the growth rate, see Section 5.4 Growth rate and 5.6 Reaction order. This means that the incorporation rate of boron will be almost constant as a function of temperature but the supply of carbon growth species will increase which increases the growth rate. This will decrease the boron/carbon ratio in the growing film. When the deposition process enters the transport limited regime at temperatures above 675 °C the supply of carbon growth species will also be diffusion limited. This explains why the boron carrier concentration levels off to constant values at the highest temperatures but not why the carrier concentration increases just above 675 °C. One reason for this increase in the boron/carbon ratio may be that the growth rate at the same time decreases. If one assumes that the incorporation rate of boron is constant this
can explain the trends. One should, however, be careful since the doping levels calculated by MSP also depends on the surface area of the diamond film.

5.6 Reaction order

The growth rate at a constant temperature can expressed by the reaction order according to:

\[
r = k[\text{CH}_4]^x[\text{TMB}]^y[\text{H}_2]^z
\]

Eq.15

where [\text{CH}_4], [\text{TMB}] and [\text{H}_2] expresses concentrations or partial pressures and \(x, y\) and \(z\) are the reaction orders for each precursor, respectively. Since all the precursors introduced into the chamber are directly controlled by a mass flow controller (no evaporator was used), the gas concentrations can then be represented as partial pressures (or mass flow). Moreover, since \(\text{H}_2\) constitutes more than 99% of the gas phase, it will be treated as constant during the experiments. Thus, the reaction order is determined by the slope of a linearized plot based on the TMB and \(\text{CH}_4\) concentration using in Eq.15. The reaction order of \(\text{CH}_4\) was obtained by using a constant flow rate of TMB equal to 0.01 SCCM, see Figure 19. Meanwhile, the reaction order of TMB was obtained in a similar way with constant \(\text{CH}_4\) flow of 0.5 and 1 SCCM, see Figure 20. All reaction orders were calculated from the kinetically controlled regime.

Thus, from Figure 19 a reaction order for \(\text{CH}_4\) is 0.94. This value is close to 1 which means a linear growth rate. This is similar to the findings of Corrat’s study [108] that the methyl radical incorporation reaction should be proportional to the \(\text{CH}_4\) concentration in the gas phase. This linear growth rate vs. \(\text{CH}_4\) concentration has also been observed by others [109, 110]. This reaction order supports the theory that \(\text{CH}_3\) radicals are the main growth specie in HFCVD of diamond.

Since TMB contains three methyl groups, it will produce methyl radical in the CVD process thus contributing with carbon containing growth species. The TMB/\(\text{CH}_4\) ratio is only around 1 % so this contribution must be small in this case. Thus, in the kinetically controlled regime (i.e., below 675°C), the growth rate will increase slightly with increasing TMB flow rate which has been shown in the Section 5.4 Growth rate. It is difficult to draw any conclusions about this contribution since the increase is within the error limits of the experiments. Anyhow, the reaction order for TMB is very close to 0 (0.04 – 0.07), see Figure 20. One conclusion is that TMB does not affect the mechanism of the HFCVD of boron doped diamond at a measurable level.
Figure 19. Reaction order plot of the logarithm of the thickness vs. the logarithm of the partial pressure of CH$_4$. The inset value is the reaction order of CH$_4$. Plotted are the respective substrate temperature: 625 °C (black squares), 650 °C (red circles) and 675 °C (blue triangles).

Figure 20. Reaction order plot of the logarithm of the thickness vs. the logarithm of the partial pressure of TMB. The inset value is the reaction order of TMB. Plotted are the respective substrate temperature: 625 °C (black squares), 650 °C (red circles) and 675 °C (blue triangles).
6 Concluding remarks

It has experimentally been observed that the addition of a dopant species in the gas phase have a strong effect on the CVD growth process – either positive or negative depending on the dopant species. However, it is difficult to extract the information about the underlying causes to the observations from experiments. The present theoretical study has therefore focused on high-level DFT calculations in order to investigate the effect on diamond growth by various dopants. The four main dopants are nitrogen, phosphorous, sulphur and boron, were carefully studied within the lattice of H – terminated diamond (111), (110) and (100)-2×1, respectively. The results have been compared with the non-doped scenario in order to prove and explain the experimental observation that either an increase, or decrease, in growth rate will be obtained for different doping situations.

The theoretical study is based on the assumption that hydrogen abstraction from the surface is a growth rate limiting reaction step. This abstraction of surface hydrogen atoms has therefore been studied from both a thermodynamic and a kinetic point of view. The information about the driving force of the hydrogen abstraction process was calculated from the abstraction energies, while on the other hand, the information about the growth rate was calculated from the abstraction energy barriers.

The hydrogen abstraction energies and the hydrogen abstraction energy barriers for different diamond surfaces were first investigated in Paper I for a non-doped scenario. The effect on the hydrogen abstraction energies and the hydrogen abstraction energy barriers by nitrogen (Paper I), phosphorous (Paper II), sulphur (Paper II) and boron (Paper III) substitutionally present in different atomic carbon layer, were then studied by comparing with the non-doped scenario. The results show that there is a significant increase in surface reactivity, and thereby decrease in abstraction energy barrier (to zero), with nitrogen and phosphorous present in the lattice. However, the situation with sulphur and boron shows different results in that the surface reactivity will increase only for sulphur positioned within the 4th atomic carbon layer and boron within the 2nd atomic carbon layer. A reduction in surface reactivity, and thereby a larger abstraction energy barrier, was found for these two dopants (sulphur and boron) in the other carbon layers. Moreover, a local effect (laterally seen) has been shown for phosphorous and boron doping which means that the abstraction energy will energetically be the most preferred one when the hydrogen abstraction site is closest to the
dopant. This local effect is obvious for especially phosphorous and boron doping within the 2\textsuperscript{nd} atomic carbon layer, where the interaction between the incoming hydrogen radical and the surface hydrogen atom is strong enough for a direct formation of a hydrogen molecule. For sulphur doping within the 4\textsuperscript{th} atomic carbon layer, a less local effect was observed, in that the hydrogen abstraction energy did only change slightly when latteraly moving the surface reaction site away from the sulphur dopant position.

Based on these theoretical results, and compared with non-doped diamond scenario, it can be concluded that the growth rate will increase for phosphorous and nitrogen doping while it can both increase and decrease depending on the layer position for sulphur and boron doping. These calculated phenomena do strongly support the experimental observations. Thus, it is possible to tailor-make and develop novel dopant systems for higher diamond deposition rates and/or lower deposition temperature with these deeper knowledge of the effect by various dopants on the diamond growth.

In addition, in Paper IV, an experiment was carried out to investigate the effect of TMB on the growth mechanism of boron doped diamond. The results show that TMB does not affect the growth of the HFCVD of boron doped diamond due to the linear diamond growth rate with CH\textsubscript{4} concentration. However, the boron carrier concentration is depending on the total mass flow of TMB but it is also sensitive to the substrate temperature which is correlated to the two different growth mechanisms.

Diamant är dessutom kemiskt inert, vilket gör materialet användbart i starkt korrosiva miljöer. På grund av det stora bandgapet hos diamant (5.45 eV), så har materialet alltid betraktats som en isolator. Emellertid, möjligheten att dopa med olika dopelement gör att diamant får extraordinära elektroniska egenskaper, som exempelvis en hög laddningsmobilitet.

Om man även lägger till det breda elektrokemiska fönstret så har diamant helt nyligen kommit att betraktas som en lovande kandidat för tillämpningar i olika typer av elektronisk apparatur. Det har också helt nyligen befunnits att diamant är biokompatibelt med biologiska vävnader, vilket öppnar upp för användbarhet inom biomedicinska tillämpningar. Emellertid, för att lyckas med diamant som material inom alla dessa tillämpningar så måste tillväxten ytterligare förfinas samt förbättras.

Fyra dopämnen har använts i denna studie (N, P, S och B), vilka har ersatt C i kristall-gittret för H–terminerade diamond (111)-, (110)- och (100)-2×1-ytor. De erhållna resultaten har jämförts med motsvarande resultat för odopade diamant-ytor. Detta har gjorts i syfte att förklara de experimentella observationer där man antingen får en ökning eller minskning av tillväxthastigheten, beroende på dopämne och plats i diamant-gittret.


En lokal lateral effekt har också påvisats för P- och B-dopning vilket betyder att H-abstraktionsenergin är mest gynnsam för situationen med en abstractions-plats som är närmast dopämnet. Denna lokala effekt är tydligast för P- och B-dopning inom the andra C-lagret. Dessutom, interaktionen mellan det inkommande radikala gasfas-vätet och det bundna vätet till ytan är så pass stark att en vätemolekyl bildas automatiskt.

För S-dopning inom det fjärde C-lagret så kunde man också påvisa en mer lokal effekt i och med att H-abstraktionsenergin minskade gradvis ju längre ifrån det ytbindna vätet var dopämnet S.

Baserat på dessa teoretiska resultat, och i jämförelse med situationen utan dopning, kan man konstatera att man får en ökning av tillväxthastigheten för N- och P-dopning. Dessutom, man kan antingen få en minskning eller ökning under användandet av S- eller B-dopämne.

Dessa beräknade resultat kopplas starkt till experimentella observationer. Det har därmed visat sig möjligt att skräddarsy dopsystem för att erhålla en högre beläggningstid och/eller en lägre deponeringstemperatur under användandet av CVD-deponering av diamant.

också känslig för substrat-temperaturen, vilket korrelerar till de två olika
tillväxtmekanismerna.
First of all, I would like to address my appreciation to my main supervisor, Professor Karin Larsson, for giving me guidance and encouragement over the years. Thank you for your ideas and enthusiasm, your advice and support. From you, I have learned how to study in theoretical chemistry for simulating diamond growth, and how to be a great scientist.

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9 References


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