The Combined Influence of Dopant Species and Surface Termination on the Electronic Properties of Diamond Surfaces

Karin Larsson

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Abstract: The combined effects of geometrical structure and chemical composition on the diamond surface electronic structures have been investigated in the present study by using high-level theoretical calculations. The effects of diamond surface planes [(111) vs. (100)], surface terminations (H, F, OH, O_{ontop}, O_{bridge}, vs. NH$_2$), and substitutional doping (B, N vs. P), were of the largest interest to study. As a measure of different electronic structures, the bandgaps, work functions, and electron affinities have been used. In addition to the effects by the doping elements, the different diamond surface planes [(111) vs. (100)] were also observed to cause large differences in the electronic structures. With few exceptions, this was also the case for the surface termination species. For example, O_{ontop}-termination was found to induce surface electron conductivities for all systems in the present study (except for a non-doped (100) surface). The other types of surface terminating species induced a reduction in bandgap values. The calculated bandgap ranges for the (111) surface were 3.4–5.7 (non-doping), and 0.9–5.3 (B-doping). For the (100) surface, the ranges were 0.9–5.3 (undoping) and 3.2–4.3 (B-doping). For almost all systems in the present investigation, it was found that photo-induced electron emission cannot take place. The only exception is the non-doped NH$_2$-terminated diamond (111) surface, for which a direct photo-induced electron emission is possible.

Keywords: diamond; doping; surface termination; electronic structure; band gap; work function; electron affinity; electron emission

1. Introduction

Diamond is a well-studied material with extraordinary properties. It has excellent mechanical, thermal, chemical, electrical, electrochemical, and optical properties (e.g., high hardness, low coefficient of friction, good wear resistance, low thermal expansion coefficient, high thermal conductivity, excellent chemical inertness, high charge carrier mobility, low background current, favorable optical transparency, etc.). In addition, it shows quite unique electrochemical properties, such as a large electrochemical potential window, a low dielectric constant, controllable surface termination, and a high breakdown voltage [1]. However, the large band gap (5.4 eV) makes diamond an insulator, which thereby limits the usage of diamond for, e.g., electronic devices. However, it is possible to improve the diamond electronic properties substituting some C atoms with dopant elements. Another way is to terminate the diamond surfaces with specific atomic (or molecular) species. Hence, a change in the electron density, especially in the vicinity to the diamond surface, will induce the necessary electronic bandgap structure for, e.g., those applications where diamond is a plausible electrode material.

More generally, the properties of a crystalline solid surface depend on various factors, such as (i) number and distribution of binding atoms (i.e., for the atoms in the surface region), (ii) surface reconstructing and relaxation, (iii) type and degree of chemisorption to the surface, and (iv) elemental
doping within the upper surface region. The number and distribution of binding atoms to a surface atom (i) is always different to the situation with bulk atoms, making this surface atom more reactive (since it has the driving force to become bulk-like). In addition, the factors (ii)–(iv) do also represent changes in the surrounding electron density for the surface atoms, which are all different from the situations with bulk atoms. Variations of all these factors can, thus, make it possible to adjust the surface electronic properties, which is not in the same way possible for the corresponding bulk material. For diamond surfaces, examples of electronic properties that are of major interest for many applications are bandgap states, work function, (photo-induced) emission of electrons, and electron affinity.

Experimentally obtained electronic properties (e.g., work function) have been found to be different depending on the type of diamond material (i.e., single crystalline diamond (SCD), microcrystalline diamond (MCD), nanocrystalline diamond (NCD), or ultrananocrystalline (UNCD)). Another material is the novel Q-carbon phase, which consists of quenched amorphous carbon with numerous randomly oriented tetrahedra. For undoped diamond, an H-terminated single crystalline (100) surface showed an ionization energy value of 4.2 eV [2] (the ionization energy is comparable to the work function). However, the work function was estimated to be 3.3 eV for H-terminated NCD [3]. The situations were similar for the doped diamond surfaces. For n-type doping with nitrogen, a range from 1.29 to ~2 eV was reported for UNCD [4,5]. For NCD this range was <2 to 3.3 eV [6], and for MCD it was 1.44 to 2.22 eV [4,7–9]. Moreover, work function values of 1.8 and 2.23 eV were obtained for PCD and NCD, respectively [10]. The work function for a highly P-doped (111) surface of SCD has also been estimated, and it was found to be of size ~3.8 eV for an H-terminated surface, and of size ~3.9 eV for an O-terminated surface [11]. Moreover, the field emission characterization of a heavily P-doped H-terminated diamond (111) surface resulted in a P donor level ~0.6 eV below the VBM [12]. A donor level at 2.3 eV below VBM was also observed for NCD [13]. Furthermore, the novel Q-carbon phase shows an outstanding electron emission property. It has a very low work function, which promotes the excellent electron emission behavior [14–16].

Since the diamond electronic properties varies with the type of material, there is a need to obtain a deeper knowledge about the electronic properties of diamond with controlled structural geometries (such as single crystalline diamond). Theoretical simulations can offer this possibility. Theoretical modelling techniques have during the last decades been dramatically developed. By using these theoretical methods, it is possible to acquire information about the effects of factors like (i) diamond surface plane, (ii) types of surface terminations, and (iii) substitutional doping on various electronic properties. First principle DFT techniques are the most frequently used methods in studying properties like work function, electron affinity, and photo-induced electron emission. It must though be stressed, that it is not only possible to calculate these various properties on an atomic level, it is also possible to acquire a deeper underlying knowledge about the causes to these observations. Consequently, it is possible to tailor-make materials with specific electronic properties by using theoretical modelling tools in combination with experimental activities.

The purpose of the present work is to study the combined effect of substitutional doping and surface termination on the bandgap electronic structure of diamond (111) and 2 × 1-reconstructed (100), respectively. The doping elements include both n-type dopants (N and P), and a p-type dopant (B). In addition, the terminating species include H, F, OH, O, and NH₂. From the knowledge concerning the electronic structures in the energy region around the respective bandgaps, it has been shown possible to gain information about important electronic properties like electron affinity, work function, as well as possibilities for photo-induced electron emissions.

2. Theoretical Methods

All calculations in the present study were performed using density functional theory (DFT) under periodic boundary conditions [17]. The geometrical structures of the various model systems where obtained by performing constrained geometry optimization (see Section 2. Model Systems), using the BFGS algorithm (Broyden-Fletcher-Goldfarb-Sharma) [18] within the Cambridge Sequential Total Energy
Package (CASTEP) software from BIOVIA [19–21]. More specifically, an ultrasoft pseudopotential [22] plane-wave approach was thereby used, which is based on the PBE (Perdew-Burke-Ernzerhof) [17] generalized gradient approximation (GGA) [19] of the exchange-correlation functional. Because of the presence of unpaired electrons in the systems, all calculations were based on spin polarized GGA (i.e., GGSA). In addition, the value of the energy cutoff for the plane wave basis set was set to 370.00 eV. Moreover, the Monkhorst-Pack scheme [23] was used for the k-point sampling of the Brillouin zone, which generated a uniform mesh of k points in reciprocal space. The $1 \times 1 \times 1$ k-point, as well as the cut-off frequency of 370 eV, have earlier been tested and found adequate to use for the present type of system [24,25].

The CASTEP program, with the setting presented above, was also used in calculating the density difference when adding the terminating species to the non-terminated diamond surface (undoped or doped) (see Equation (1)):

$$\Delta \rho = \rho_{\text{total}} - \left( \rho_{\text{bare surface}} + \rho_{\text{adsorbate layer}} \right) \quad (1)$$

where $\Delta \rho$ is the density difference, and $\rho_{\text{total}}$, $\rho_{\text{bare surface}}$, and $\rho_{\text{adsorbate layer}}$ are the electron densities for the terminated surface, non-terminated surface, and complete adsorbate layer, respectively. The geometry-optimized structures were used for these single point calculations (i.e., with no geometry optimization). The results from these calculations show the re-positioning of electron density, being induced by surface termination. For example, weakening (or strengthening) of bonds will thereby be illuminated. Other examples are induced dipoles at the surface.

The CASTEP program was also used in calculating electron bond populations and atomic charges, which are the two parameters that will give further insight into eventual bond weakening/strengthening (using electron bond populations) and dipole formations (using atomic charges). The assigned atomic charges were Mulliken charges since the alternative, the Hirsfield charges, often underestimates charges distributions in molecules [26]. In assigning the Mulliken atomic charges, as well as the bond population values, a projection of the plane wave states onto the localized basis was made by using a technique described by Sanchez-Portal et al. [23].

The electronic structure, including valence band maximum (VBM), conduction band minimum (CBM), bandgap and bandgap electronic states, were calculated using the software Atomistix Toolkit 2018.1 from Synopsys [27]. These DFT calculations were based on a spin-polarized generalized gradient approximation (GGSA) [17,20], using the PBE pseudopotential in addition to a linear combination of atomic orbitals (LCAO). Moreover, a Monkhorst-Pack k-point sampling of $5 \times 5 \times 1$ was used in calculating both the electron band structures (i.e., DOS (Density Of State) spectra, band structures and fat-bandstructure). The fat-band structure is just another name of the projected band structure, which was used to visualize the contribution of different atoms to the band structures of the various model systems in the present study. Also, the density mesh cut-off was set to 80 Ha (2176, 8 eV). The well-known problem with the DFT-calculations is the underestimation of bandgap values. The GGA-1/2 method [28] was therefore used in the present investigation. This method is a semi-empirical approach to correct the self-interaction error in local and semi-local exchange-correlation density functionals for extended systems. As such, it corrects the Kohn-Sham eigenvalues around the bottom of the conduction band and the top of the valence band. Test-calculations were performed by calculating the bandgap for bulk diamond, and to comparing these results with the experimentally obtained ones. The here presented method resulted in a bulk diamond bandgap of 5.6 eV, which is almost identical with the experimental one: 5.5 eV.

Calculated VBM values give information about the work functions of the studied model systems, and the calculated CBM values give information about the electron affinities. In addition, calculated electronic states in the bandgap give information about the possibility for photo-induced electron
emission. The work function is defined as the minimum energy needed to remove an electron from VBM to the vacuum outside the surface (see Equation (2)):

$$\text{Work function (}\phi) = E(\infty) - E_{\text{VBM}}$$  \hspace{1cm} (2)

where $E(\infty)$ is equal to zero, and $E_{\text{VBM}}$ is the energy of the VBM. Moreover, the electron affinity (EA) is defined as (see Equation (3)):

$$E_{\text{A}} = E(\infty) - E_{\text{CBM}}$$  \hspace{1cm} (3)

where $E(\infty)$ is equal to zero, and $E_{\text{CBM}}$ is the energy of the CBM.

The program Dmol3 [29,30] from BIOVIA was in the present study used for calculations of the valence band maximum, and thereby also the work function. A GGA method, which was based on a PBE non-local functional, was then applied. All electrons in the systems were included in these calculations, in addition to a DNP (double numerical potential) atomic orbital basis set. DNP is a polarized function with an angular momentum that is larger than that of the highest occupied orbital in the free atom. It gives a relatively more reliable description of the electronic structure of the systems under investigation [29].

3. Model Systems

The (111) and the 2×1-reconstructed (100) surfaces are the most frequently observed ones on the nano-diamond particles and nanocrystalline diamond. It has earlier been theoretically shown that it is possible to model (111) and (100) surfaces of nanodiamond particles of size larger than ~2 nm by using 2D model slabs [31]. The diamond (111) and (100)-2×1 surfaces have therefore been chosen in studying the diamond surface electronic properties in the present study. The supercell model of the (111) surface include 6 C layers, with 16 C atoms in each layer. The corresponding (100) model include 7 C layers, with 16 C atoms in each layer. These model sizes have earlier been found large enough for the present type of study [32]. Moreover, the model surfaces are terminated with various types of species; H, F, OH, O, and NH$_2$, respectively. All species are adsorbed in ontop positions (i.e., directly on a surface C atom), and O are also adsorbed on a bridge position (see Figure 1). The various positions of O are therefore denoted O$_{\text{ontop}}$ and O$_{\text{bridge}}$. Moreover, in the doped diamond models, the dopant has substitutionally replaced a C atom in the lattice. It has earlier been shown that a dopant substitution within the second C layer will have the largest effect on the diamond surface electronic structure [32–34]. This position of any of the dopants B, N, or P, has therefore been chosen in the present study. In addition, the lower surface C atoms have been terminated with H atoms. The purpose with this choice was to saturate the radical C atoms on this lower surface. In addition, both the lower C atoms and their terminating H atoms were kept fixed in the geometry optimization calculations. The other atoms, in the model systems, could freely relax (see Section 2. Theoretical Methods). The reason for these geometrical constraints was to simulate a continuation into bulk diamond. Moreover, a large vacuum distance between the slabs was used (>15 Å) in order to avoid inter slab interactions. This is a distance that earlier has been tested and found adequate to use for the present types of systems [32].
The electronegativity of the chemisorbed species will thereby influence the emission current and threshold voltage [35]. The phenomena of diamond surface termination have experimentally also been observed to significantly influence the broad-band infrared reflectivity [36]. Hydrogen-terminated diamond surfaces have been found to be hydrophobic [37] and to show unique p-type surface electronic conductivity [38]. The oxygen atom is also one of the most used diamond surface terminators. Oxygen-terminated diamond surfaces generally show hydrophilic properties [39], as well as a positive electron affinity. The oxygen-termination can appear as a surface binding OH, O_{bridge}, C_{ontop}, or OOH groups. Different chemical routes are used to link functional groups to these O-group adsorbates. This procedure is usually performed in e.g., electroanalytical applications [40]. Fluorine-termination will, compared to H-termination, result in an even more hydrophobic diamond surface. In addition, F-terminated diamond surfaces exhibit exceptional electrochemical properties, such as a lower electrocatalytic activity, a wide electrochemical potential window, and low background current [41,42]. Nitrogen-terminated diamond surfaces are generally very chemically reactive and are thereby commonly used as an intermediate for further modification of the diamond surface (e.g., as a linker). For instance, a diamond surface that is terminated with amine (NH$_2$) can be modified to be used as a functionalized surface in biosensors [43].

5. Substitutional Doping of Diamond

The boron atom is one of the most used p-type dopants. B-doped diamond shows quite promising electrochemical properties, e.g., tunable electronic conductivity (depending on the boron-carrier concentration in the diamond lattice). Hence, boron-doped diamond (BDD) has been widely used for electronic applications. Nitrogen, as an n-type dopant, has also frequently been studied during the last decades [44–48]. However, the deep donor level of nitrogen (1.7 eV below the conduction band) limits the usage of nitrogen-doped diamond as an effective n-type semiconductor. Thus, phosphorous has
instead been introduced as a plausible n-type donor in diamond (111) [49]. Kato et al. produced this type of n-type diamond epilayer on (100)-oriented diamond surfaces [50]. Phosphorus, P, is nowadays the only well-established substitutional n-type donor [51]. n-type diamond heavily doped with P atoms, has recently been obtained with low electrical resistivity and low incorporation activation energy [52,53]. This makes phosphorus-doped diamond more promising for device applications, e.g., as an electron source for bipolar devices [54–56], as Schottky barrier diodes [57], and for thermionic emission applications [58].

6. Effect of Surface Terminating Species on the Surface Electronic Structure

6.1. General

The chemisorption of atoms (or molecules) to the diamond surface will lower the surface energy values, which will affect the chemical surface processes. It is also expected that the chemisorption (i.e., termination) of species to the surface will have a major effect on the properties of the surface (e.g., surface electronic properties). Despite the efficiency in upholding the cubic structure of the diamond surface, different types of surface termination species have been shown to change the properties of the diamond surface region (e.g., by inducing surface electronic conductivity and interfacial charge transfer properties). Another example of properties that may be affected by chemisorption is the field emission characteristics. The electronegativity of the chemisorbed species will thereby influence the emission current and threshold voltage [35]. The phenomena of diamond surface termination have experimentally also been observed to significantly influence the broad-band infrared reflectivity [36]. Hydrogen-terminated diamond surfaces have been found to be hydrophobic [37], and to show unique p-type surface electronic conductivity [38]. On the other hand, oxygen-terminated diamond surfaces generally show hydrophilic properties [37], and exhibit positive electron affinity [59]. In addition, OH-terminated surfaces can be formed during etching in a mixture of oxygen and water vapor [39]. Fluorine-termination will, compared to H-termination, result in even more strongly hydrophobic diamond surfaces, and have also recently been found to enhance the sp³ characteristics of the diamond upper C layer (thereby improving the geometrical structure of this surface [60]). All these interesting properties of terminated diamond surfaces make it clear that surface termination is very important for especially those applications where diamond can be an electrode material.

6.2. Analysis of Calculated Electronic Structures for Undoped Diamond Surfaces

The electronic states around the bandgap for various terminated diamond (111) and (100) surfaces have been investigated in the present study by calculating the band structure, projected band structure (on specific atoms), and DOS spectra for the upper region of the diamond surfaces. For each model system, this upper region included the three upper C atomic layers, in addition to the terminating one. It is clear, from the analysis of the projected band structure, that the valence orbitals of the terminating species will form hybridization with the orbitals of the surface C atoms. This is the situation for all terminating species that have been investigated in the present study (H, F, OH, O(ontop), O(bridge), and NH₂), and for both types of diamond surface plane ((111) and (100)).

As can be seen in Tables 1 and 2, the electronic structures are much different for the (111) and (100)-2 × 1 surfaces. These differences can be exemplified by the bandgap (BG) values. The BG is bulklike for an F-terminated (111) surface, while it is much smaller for the (100)-2 × 1 surfaces (with a difference of 2.5 eV: 5.5 vs. 3.0 eV). The BG value is also bulk-like for the H-terminated (111) surface, with a somewhat smaller value for the corresponding (100)-2 × 1 surfaces (with a difference of 0.6 eV: 5.4 vs. 4.8 eV). The BG values for the other terminating species (OH, O(bridge), O(ontop), and NH₂) are all smaller (to various extents) than the BG value for bulk diamond (5.47 eV). Moreover, for the NH₂- and OH-terminating species, the BG values became 3.4 eV vs. 4.6 eV [(111)] and 4.6 vs. 5.3 eV [(100)-2 × 1]. It is not energetically feasible to bind O in bridge position on the (111) surface, so any comparison between the two different surface planes is not possible here. However, the BG value for
$O_{\text{bridge}}$-termination on the (100)-2×1 surfaces was found to be 4.2 eV, which is almost identical to the BG value for NH$_2$-termination to this surface plane.

**Table 1.** Calculated values of valence band maxima, conduction band minima, bandgaps, electron affinities, and work functions for X-terminated non- or B-doped diamond (111) surfaces. X = H, F, OH, O$_{\text{ontop}}$, and NH$_2$. The energy unit is eV.

| (111) | Valence Band Maximum (VBM) | Conduction Band Minimum (CBM) | Bandgap (BG) | Electron Affinity (EA) | Work Function ($\Phi$) |
|-------|---------------------------|-------------------------------|--------------|------------------------|-----------------------|
| Non-doping | | | | | |
| H | -4.4 | +1.0 | 5.4 | -1.0 | 4.4 |
| F | -5.8 | -0.1 | 5.7 | +0.1 | 5.8 |
| OH | -4.3 | -0.3 | 4.6 | +0.3 | 4.3 |
| O$_{\text{ontop}}$ | -5.4 | -4.9 | 0.5 | +4.9 | 5.4 |
| NH$_2$ | -2.8 | +0.7 | 3.4 | -0.7 | 2.8 |
| B-doping | | | | | |
| H | -3.2 | +0.3 | 3.5 | -0.3 | 3.2 |
| F | -5.3 | 0 | 5.3 | -0 | 5.3 |
| OH | -3.6 | 0.9 | 4.5 | -0.9 | 3.6 |
| O$_{\text{ontop}}$ | -5.4 | -5.0 | 0.4 | +5.0 | 5.4 |
| NH$_2$ | -2.7 | -1.8 | 0.9 | +1.8 | 2.7 |
| N-doping | | | | | |
| H | -4.6 | -4.3 | 0.3 | +4.3 | 4.6 |
| F | -5.9 | -5.6 | 0.3 | +5.6 | 5.9 |
| OH | -4.6 | -4.2 | 0.5 | +4.2 | 4.6 |
| O$_{\text{ontop}}$ | -5.4 | -5.0 | 0.3 | +5.0 | 5.4 |
| NH$_2$ | -3.1 | -2.7 | 0.4 | -2.7 | 3.1 |
| P-doping | | | | | |
| H | -4.9 | -4.2 | 0.6 | +4.2 | 4.9 |
| F | -6.1 | -5.1 | 1.0 | +5.1 | 6.1 |
| OH | -4.8 | -4.3 | 0.5 | +4.3 | 4.8 |
| O$_{\text{ontop}}$ | -5.4 | -5.0 | 0.4 | +5.0 | 5.4 |
| NH$_2$ | -3.7 | -3.4 | 0.3 | +3.4 | 3.7 |

The only exception to the dissimilarities between the two diamond surfaces is the situations with the O$_{\text{ontop}}$-termination. Supercell models of these surfaces are shown in Figure 2. The BG values became as small as 0.5 eV [(111)] and 0.9 eV [(100)] [it is here very interesting to also note that the BG values for NH$_2$, O$_{\text{ontop}}$, and OH-terminated diamond (100) surfaces are also very similar]. As can be seen in the DOS spectra in Figure 3a,b, the O$_{\text{ontop}}$-terminated (111) surface can, however, be regarded as electronic conductive, while the O$_{\text{ontop}}$-terminated (100) cannot. For the (111) surface, the $E_{\text{Fermi}}$ is positioned within the valence electron band, while the $E_{\text{Fermi}}$ for (100) is positioned within the bandgap. These differences in electronic properties have its origin in the difference in geometrical surface structures. For the (111) surface, the O$_{\text{ontop}}$-termination will result in radical O adsorbates with covalent single bonds to the upper surface C atoms (see Figure 2a). This radical nature comes from the fact that O atoms have 6 valence electrons. The reactions between the O species and the radical surface C atoms on the diamond (111) surface, that lead to single bonded C–O formations, will therefore
result in radical O atoms. However, rather weak spin-densities could be found (see Figure 4a). This is most probably due to the withdrawal of electron density from the surface C atoms to the binding O atoms (induced by the large difference in electronegativity). This addition in electron density will contribute to partially paired electrons on the O adsorbates, thereby reducing the spin density within the terminating layer. Moreover, these partially unpaired electrons will form a broad and non-filled energy band which is a strong indication of surface electronic conductivity (see Figure 3a).

Table 2. Calculated values of valence band maxima, conduction band minima, bandgaps, electron affinities, and work functions for X-terminated non- or B-doped diamond (100) surfaces. X = H, F, OH, O\textsubscript{ontop}, O\textsubscript{bridge}, and NH\textsubscript{2}. The energy unit is eV.

|          | (100) | Valence Band Maximum (VBM) | Conduction Band Minim (CBM) | Band Gap (BG) | Electron Affinity (EA) | Work Function (\(\Phi\)) |
|----------|-------|----------------------------|----------------------------|---------------|------------------------|--------------------------|
| Non-doping | H     | −3.9                       | +0.9                       | 4.8           | −0.9                   | 3.9                      |
|          | F     | −4.8                       | −1.8                       | 3.0           | +1.8                   | 4.8                      |
|          | OH    | −4.9                       | +0.4                       | 5.3           | −0.4                   | 4.9                      |
|          | O\textsubscript{ontop} | −5.0                       | −4.2                       | 0.8           | +4.2                   | 5.0                      |
|          | O\textsubscript{bridge} | −4.7                       | −0.5                       | 4.2           | +0.5                   | 4.7                      |
|          | NH\textsubscript{2} | −3.7                       | +0.8                       | 4.5           | −0.8                   | 3.7                      |
| B-doping | H     | −3.4                       | +0.6                       | 4.0           | −0.6                   | 3.4                      |
|          | F     | −5.0                       | −0.7                       | 4.3           | +0.7                   | 5.0                      |
|          | OH    | −4.0                       | +0.1                       | 4.1           | −0.1                   | 4.0                      |
|          | O\textsubscript{ontop} | −5.0                       | −4.7                       | 0.3           | +4.7                   | 5.0                      |
|          | O\textsubscript{bridge} | −4.7                       | −1.5                       | 3.2           | +1.5                   | 4.7                      |
|          | NH\textsubscript{2} | −3.2                       | +0.8                       | 4.0           | −0.8                   | 3.2                      |
| N-doping | H     | −3.7                       | −3.5                       | 0.2           | +3.5                   | 3.7                      |
|          | F     | −5.3                       | −5.0                       | 0.2           | +5.0                   | 5.3                      |
|          | OH    | −4.2                       | −3.9                       | 0.2           | +3.9                   | 4.2                      |
|          | O\textsubscript{ontop} | −5.3                       | −5.0                       | 0.3           | +5.0                   | 5.1                      |
|          | O\textsubscript{bridge} | −3.7                       | −1.3                       | 2.4           | +1.3                   | 3.7                      |
|          | NH\textsubscript{2} | −3.8                       | −3.7                       | 0.1           | −3.7                   | 3.8                      |
| P-doping | H     | −4.0                       | −2.9                       | 1.1           | +2.9                   | 4.0                      |
|          | F     | −5.5                       | −4.3                       | 1.2           | +4.3                   | 5.5                      |
|          | OH    | −4.5                       | −4.2                       | 0.3           | +4.2                   | 4.5                      |
|          | O\textsubscript{ontop} | −5.3                       | −5.2                       | 0.1           | +5.2                   | 5.3                      |
|          | O\textsubscript{bridge} | −4.0                       | −1.9                       | 2.1           | +1.9                   | 4.0                      |
|          | NH\textsubscript{2} | −4.1                       | −4.0                       | 0.9           | +4.0                   | 4.1                      |
The situation is completely different for the (100) surface. Adsorption of O species to ontop-positions on the 2 × 1-reconstructed (100) surface will induce a surface re-construction to the (100) surface (Figure 2b). The original C–C bonds within the 2 × 1-reconstructed surface has thereby been disrupted, leaving surface radical C atoms with two “dangling bonds” each. The hereby formed unpaired C electrons can now pair with the unpaired electrons in the O_{ontop} adsorbates, forming very strong C=O bonds. These surface regions are, therefore, not expected to be radical to its nature. As demonstrated by the spin-density map in Figure 4b, there is just a weak tendency for radical formation. Also, this observation is most probably due to the withdrawal of electron density from the surface C atoms to the binding O atoms. Moreover, the calculated C–O bond populations indicate much stronger covalent bonds. These values are of size 1.2, which is almost double the size when compared with the corresponding C–O bonds for the O_{ontop}-terminated (111) surface (0.8). Hence, no unfilled energy band is expected to be formed for this type of surface.

Calculations of the valence band maxima (VBM) did also result in different numerical values for the two diamond surface planes. The absolute values of the VBMs are identical to the work functions, \( \Phi \) experimentally shown to lower the ionization energy (i.e., the work function) to a value of 4.2 eV for the (100) surface [2]. This is a value that is very similar to the here presented calculated value of 3.9 eV.

**Figure 2.** Resulting geometries after structural relaxation of non-doped O_{ontop}-terminated (a) (111) and (b) (100) surfaces. (For clarity, a magnified view of a part of the surface is shown for the (100) surface). Grey: carbon; white: hydrogen; red: oxygen.
Figure 3. Calculated DOS spectra for non-doped O_{ontop}-terminated (a) (111) and (b) (100) surfaces. The spectra cover the upper surface parts (i.e., O_{ontop}-terminating layer, and C atoms in the upper two atomic layers). The unit of the x-axis is eV, and the unit of the y-axis is electron density. The Fermi level is positioned at 0 eV. Blue—s-states; Orange—p-states.
Figure 4. Calculated spin-density maps for non-doped O$_{\text{ontop}}$-terminated (a) (111) and (b) (100) surfaces. The iso-surface value is 0.002 and 0.05 for the diamond (111) and (100) surface, respectively. The blue color shows the positive density, and the yellow color shows the negative density.

From the calculated values of VBM's and BGs it was also possible to calculate the electron affinities (EAs) for the variously terminated diamond surfaces. As can be seen in Table 1 that H- and NH$_2$-terminated diamond (111) surfaces show negative electron affinities (NEA), while F- and OH-termination result in positive electron affinities (PEAs). As expected, the situation was also here different for the diamond (100) surface (see Table 2). The H-, OH-, or NH$_2$-terminated (100) surface show NEAs, while the others (F-, O$_{\text{bridge}}$, and O$_{\text{ontop}}$-termination) will render PEAs. The electron affinities of H- and O-terminated diamond (100) surfaces have been experimentally estimated by using a combination of work function and photoemission experiments [59]. The obtained EA values were -1.3 for H-termination and +1.7 eV for O-termination. These values are to be compared with the calculated EA values in the present study; -0.9 (H-termination), +0.5 (O$_{\text{bridge}}$-termination), and +4.2 (O$_{\text{ontop}}$-termination) eV). The experimental value of +1.7 eV is most probably the result of a mixture of O$_{\text{bridge}}$- and O$_{\text{ontop}}$-terminations on the (100) surface. Other experimental studies have resulted in NEA values ranging from -1.1 to -1.3 for H-terminated diamond surfaces [61]. These values are very similar to the here presented theoretical values of -0.9 eV (100) and -1.3 eV (111).

The possibilities for photo-induced electron emission, by using visible light, has also been studied in the present investigation. The difference in surface properties between diamond (100) and (111) is also very clear here. As can be seen in Tables 1 and 2, and in Figures S1 and S5, it will only be possible to induce electron emission from the NH$_2$-terminated (111) surface, and this can take place by a direct
excitation of energy size 2.8 eV (i.e., ~443 nm). For the (100) surface, there is no possibility to emit electrons by using visible light.

The electronically conductive O\textsubscript{ontop}-terminated diamond (100) surface is of no interest to study when considering electron affinities and photo-induced electron emission.

7. The Combined Effect of p-Type Doping and Surface Termination on the Surface Electronic Structure

7.1. General

The growth process of boron-doped (B-doped) diamond material, with its extraordinary electrochemical properties, has earlier been well developed. It was then found that the B dopant will increase the electronic conductivity, as compared with intrinsic non-doped diamond [62]. Depending on the dopant concentrations, the diamond material will show a metallic-type conductivity [63,64], p-type semi-conductivity [65,66], or superconductivity [67,68]. The superconductivity property makes diamond very attractive for electronic applications.

7.2. Analysis of Calculated Electronic Structures for B-Doped Diamond Surfaces

The B-induced acceptor states for diamond (111) and (100) were found to be very similar to the experimental values for B-doped bulk diamond. The positions of these states, above the respective valence band maxima, are 0.2–0.9 eV for diamond (111), and, with one exception, 0.3–0.4 eV for diamond (100). As can be seen in Tables 1 and 2, these values correspond to the following orders (with an increasing difference in energy between the acceptor state and VBM): F < O\textsubscript{ontop} < OH < H < NH\textsubscript{2} for (111), and O\textsubscript{ontop} < F = OH < H = NH\textsubscript{2} for (100). The numerical values are 0.2, 0.4, 0.5, 0.7, and 0.9 eV for (111), and 0.2, 0.3, 0.3, 0.4, and 0.4 eV for (100). The orders are very similar for the two surface planes, but with a larger spread in energy for the diamond (111) surface. Moreover, the differences in numerical values between (111) and (100) are not that large. These values are similar to the experimental results, as presented in Ref. 64; 0.2–0.37 eV. As stated above, it is only possible to terminate the (100) surface with oxygen in O\textsubscript{bridge}-positions, and for this termination situation there is a bandgap state as high as 3.2 eV above the valence band maximum. Hence, a B-doped diamond O\textsubscript{bridge}-terminated diamond (100) surface does not show any p-type conductivity.

As was the situation for non-doped diamond surfaces, there are also for the B-doped diamond (111) and (100) surfaces dissimilarities regarding the electronic structures in the energy regions around the surface bandgaps (as can be seen in Tables 1 and 2). For the (111) surface, there is an increase in BG values when going from O\textsubscript{ontop} to F (in the following trend): O\textsubscript{ontop} < NH\textsubscript{2} < H < OH < F, with the values 0.4, 0.9, 3.5, 4.5, and 5.5 eV, respectively. The corresponding values for the (100) surface show the same order: O\textsubscript{bridge} < NH\textsubscript{2} = H < OH < F, with the values 0.3, 3.2, 4.0, 4.0, 4.2, and 4.3, respectively. However, the values for the (100) surface are all very similar, which is not the case for the (111) surface. Moreover, when comparing the BG values for the different surfaces, it is only the OH species that gives similar BG values; 4.5 (111) vs. 4.2 (100) eV (see Tables 1 and 2). All of these BG values have been obtained from the DOS spectra (see Figures S2 and S6). The only exception to the dissimilarities between the two diamond surfaces is the situation with O\textsubscript{ontop}-termination. The BG values for this type of termination is as small as 0.4 eV [(111)] and 0.2 eV [(100)]. As can be seen in the DOS spectra in Figure 5a,b, both O\textsubscript{ontop}-terminated surface planes are electronically conductive. This is not the situation for non-doped diamond surfaces (see chapter 6.2. Analysis of Calculated Electronic Structures for Non-Doped Diamond Surfaces).
Figure 5. Calculated DOS spectra for B-doped O_{ontop}-terminated (a) (111) and (b) (100) surfaces. The spectra cover the upper surface parts (i.e., O_{ontop}-terminating layer, dopant, and C atoms in the upper two atomic layers). The unit of the x-axis is eV, and the unit of the y-axis is electron density. The Fermi level is positioned at 0 eV. Blue—s-states; Orange—p-states.

The B-doped diamond (111) and (100) surfaces show similar results when compared with the non-doped surfaces. As can be seen in Figure 6a, O_{ontop}-termination results in radical O adsorbates with covalent single bonds to the upper (111) surface C atoms. These unpaired electrons will also for B-doped (111) surfaces form a broad and non-filled energy band which is a strong indication of surface electronic conductivity (Figure 5a). Moreover, as was the situation with non-doped diamond (100), adsorption of O species to ontop-positions on the B-doped 2 × 1-reconstructed (100) surface was found to induce surface re-construction to (100)-1 × 1 (see Figure 6b). The B element has, compared to C, a smaller electronegativity value (2.04 vs. 2.55), and these values are both smaller than for O (3.44). There will therefore be a more pronounced transfer of electron charge from the B dopant toward the O adsorbates, which leads to larger spin densities at these surface atoms (as compared with non-doped diamond (100)) (see Figures 4b and 6b). This spin density results in a non-filled valence energy band which is a strong indication of surface electronic conductivity (Figure 5b). As is obvious from Figure 6a,b, the spins, being induced by the B dopant, result in spin-densities solely located within the terminating O layer.
With diamond (100). As can be seen in Tables 1 and 2, there are also, with the exceptions of O
ontoop (for the (100) surface) and Obridge (for the (111) surface), strong correlations with the corresponding orders
of BGs. It can here be stated that the B-doped diamond (111) and (100) surfaces show similar electronic
properties (i.e., when excluding the Oontop and Obridge scenarios).

Calculations of the valence band maxima (VBM) did also, for p-type doping (using B), result in
different numerical values for the two diamond surface planes. As can be seen in Table 1, the order of
Φ for the (111) surface became NH2 < H < OH < Oontop = F, with the values 2.7, 3.2, 3.6, 5.3, and 5.3 eV,
respectively. This order is, though, not identical to the order of BGs. However, it is identical to the
order of VBM for non-doped diamond (111), and also very similar when comparing numerical values.
Moreover, the calculated order of Φ for the (100) surface became NH2 < H < OH < Obridge < Oontop < F,
with the values 3.2, 3.4, 4.0, 4.7, 5.0, and 5.0 eV, respectively (see Table 2). There are obvious similarities
between the two different diamond surface planes. They show an identical order of work function values,
and the values for the different adsorbates are very similar when comparing diamond (111) with diamond (100).
As can be seen in Tables 1 and 2, there are also, with the exceptions of Oontop (for the (100) surface) and Obridge (for the (111) surface), strong correlations with the corresponding orders of BGs. It can here be stated that the B-doped diamond (111) and (100) surfaces show similar electronic properties (i.e., when excluding the Oontop and Obridge scenarios).

As can be seen in Table 1, H- and OH-terminated diamond (111) surfaces have negative electron
affinities, while Oontop- and NH2-termination induce positive electron affinities. For F-termination, the
electron affinity was equal to zero. The situation was, with one exception, similar for the diamond (100)
surface (see Table 2). The H-, OH-, and NH2-terminated (100) surfaces show NEA values, while the
others (F-, Obridge-, and Oontop-termination) render PEA. Total photoyield spectroscopy measurements
have shown that B-doped H-terminated polycrystalline diamond has an electron affinity of ~1.0 eV [69].
Polycrystalline diamond surfaces are comprised of (111) and (100) surface planes, and the dominating
plane depends on the experimental setup. As can be seen in Table 1, the calculated EA values for these
planes are ~0.3 eV and ~0.6 eV, respectively. These results show similarities with the experimental
values (especially for the diamond (100) surface plane).

Figure 6. Resulting geometrical structures after structural relaxation of B-doped Oontop-terminated
(a) (111) and (b) (100) surfaces. The carbon, hydrogen, oxygen, and boron atoms are shown in grey,
white, red, and pink, respectively. The calculated spin densities are also presented in the figure. The
iso-surface values are 0.002 and 0.05 for diamond (111) and (100), respectively. The blue color shows
the positive density.
As can be understood from the contents in Tables 1 and 2, as well as from the DOS spectra in Figure S2, there is no possibility to use visible light in a direct photo-induced emission of electrons from B-doped diamond surfaces [(111) or (100)].

8. The Combined Effect of n-Type Doping and Surface Termination on the Surface Electronic Structure

8.1. General

The effects of substitutional doping by nitrogen, or phosphorous, have been thoroughly studied from an experimental point of view [70–73]. It is not only the changes in the electronic properties that have been observed, but these dopant elements can also have a great impact on the diamond surface morphology and growth rate when using chemical vapor deposition methods (CVD).

The N and P elements have one additional valence electron (i.e., 5 valence electrons in total) when compared with the C atom (with its four valence electrons). When replacing C atoms in the diamond lattice with N (or P) atoms, donor states will be formed in the diamond lattice [48]. One usually calls this type of doping elements for n-type dopants, and there is an n-type doping. These n-type dopants induce a donor state just below the CBM of diamond. The valence electrons that is occupying this bandgap state, will thereby get the possibility to become thermally excited to the conduction band. The n-type doped diamond has then become a semiconducting material, with the electronic conductivity governed by electrons that originate from the donor state in the bandgap.

However, in choosing a suitable donor (or acceptor) for diamond, one has to not only consider its donor (or acceptor) level but also its solubility and mode of incorporation (e.g., incorporation during growth by in-diffusion, or by ion implantation) [48]. Impurities have been shown to become introduced into diamond during CVD or HPHT growth [74,75]. In addition, a review article has reported on doping by implantation [71]. The resulting substitutional doping will, hence, depend not only on the solubility of the impurity, but will also depend on the kinetics of the growth. Kinetic trapping may be possible although the final n- (or p-) type doped product is thermodynamically unfavorable.

8.2. Analysis of Calculated Electronic Structures for n-Type Doped Diamond Surfaces

As was the situation with non-doped diamond surfaces, there are also for the n-type doped diamond (111) and (100) surfaces dissimilarities regarding the electronic structures in the energy region around the surface bandgaps (as can be seen in Tables 1 and 2). The calculated BG values for the (111) surface, were found to be very similar for the different termination scenarios. They were found to be in the range of 0.3 to 0.5 eV for the N-doped surfaces, and 0.3 to 1.0 eV for the P-doped surfaces. For the (100) surface, the calculated BG values for the N-doped surfaces were found to be in the range of 0.1 to 0.3 eV (with one exception), and to be in the range of 0.1 and 2.0 eV for the P-doped surfaces. As the exception, the BG value for an O\textsubscript{bridge}-terminated N-doped diamond (111) surface was found to be as large as 2.4 eV. Hence, the BG values for the (100) surface are more dissimilar, as compared with the (111) surface. To be more specific, the order of BG values for the N-terminated (111) surface is H = F = O\textsubscript{ontop} < NH\textsubscript{2} < OH, with the values 0.3, 0.3, 0.3, 0.4, and 0.5 eV, respectively. On the contrary, the order of BG values for the (100) surface is NH\textsubscript{2} < H = F = OH < O\textsubscript{ontop} < O\textsubscript{bridge}, with the values 0.1, 0.2, 0.2, 0.2, 0.3, and 2.4 eV, respectively. Moreover, the order of BG values for the P-terminated (111) surface is NH\textsubscript{2} < O\textsubscript{ontop} < OH < H < F (0.3, 0.4, 0.5, 0.6, and 1.0 eV, respectively), and the different order of BG values for the (100) surface is O\textsubscript{ontop} < OH < NH\textsubscript{2} < H < F < O\textsubscript{bridge} (0.1, 0.2, 1.0, 1.1, 1.2, and 2.0 eV, respectively). These values are calculated as the difference in energy between the dopant-induced donor state and the conduction band minimum.

Moreover, there are not only differences observed between the different diamond surface planes [i.e., (111) and (100)], but also between the N- and P-doped surfaces. As can be seen in Tables 1 and 2, the BG values for the N- and P-doped diamond (111) surfaces are very similar, but they differ appreciably for the diamond (100) surface. For this latter surface plane, the order of BG values, as
well as several of the numerical values, are different when comparing the effects by the different n-type dopants. More specifically, termination by OH results in identical values, while termination by O\textsubscript{ontop} or O\textsubscript{bridge} gives values that are quite similar (less than 0.5 eV). Moreover, for H–, F– and NH\textsubscript{2}-termination, the difference in BG between N- and P-termination is as large as ~1 eV.

Experimentally, an N-donor level ~1.7 eV below the VBM has been observed for N-doped single-crystalline diamond \cite{7, 76}. Theoretically, the DOS spectra for bulk diamond does also show this feature (see Figures S3 and S7). However, the situation is completely different for the position of N in the second C layer (see Figures S4 and S8). The combined relaxation/reconstruction of the upper surface region has here resulted in an N donor level that is much closer to the VBM (See Tables 1 and 2). Moreover, field emission characterization of a heavily P-doped H-terminated diamond (111) surface have resulted in a P donor level ~0.6 eV below the VBM \cite{12}. As can be seen in Table 1, this is an experimental result that strongly supports our theoretical finding of 0.6 eV.

As was the situation with B-doped diamond (111) and (100) surfaces, the DOS calculations show that both N- and P-doped O\textsubscript{ontop}-terminated diamond (111) and (100) surfaces are electronically conductive. As compared with B-doping, substitutional doping with P was found to induce very similar geometrical structures [see Figure 2 (B-doping) and Figure 7 (P-doping)]. However, the spin-density was more pronounced when using P-doping (Figure 8). The O\textsubscript{ontop}-termination resulted in radical O adsorbates with covalent single bonds to the upper (111) surface C atoms. These unpaired electrons did thereby form a broad and non-filled energy band, which is a strong indication of surface electronic conductivity (for all P dopant concentrations). In addition, the pronounced electron transfer from the P dopant toward the O adsorbate (induced by different electronegativity values) was observed to contribute to the non-filled valence energy band, and thereby to the surface electronic conductivity.

\textbf{Figure 7.} Resulting geometrical structures after structural relaxation of P-doped O\textsubscript{ontop}-terminated (a) (111) and (b) (100) surfaces. The carbon, hydrogen, oxygen, and phosphorous atoms are shown in grey, white, red, and violet, respectively. The calculated spin densities are also presented in the figure. The iso-surface value is 0.05 for both surface planes. The blue color shows the positive density, and the yellow color shows the negative density.
Figure 7. Resulting geometrical structures after structural relaxation of P-doped O_{ontop}-terminated (a) (111) and (b) (100) surfaces. The carbon, hydrogen, oxygen, and phosphorous atoms are shown in grey, white, red, and violet, respectively. The calculated spin densities are also presented in the figure. The iso-surface value is 0.05 for both surface planes. The blue color shows the positive density, and the yellow color shows the negative density.

Figure 8. Calculated DOS spectra for P-doped O_{ontop}-terminated (a) (111) and (b) (100) surfaces. The spectra cover the upper surface parts (i.e., O_{ontop}-terminating layer, dopant, and C atoms in the upper two atomic layers). The unit of the x-axis is eV, and the unit of the y-axis is electron density. The Fermi level is positioned at 0 eV. Blue—s-states; Orange—p-states.

The situation is different for the N-doped O_{ontop}-terminated diamond (100) surface, since N is more electronegative than C: 3.04 vs. 2.55. As a consequence, the N dopant has the tendency to draw electrons from its binding C atoms, and it thereby counteracts the “neutralization” of the radical O adsorbates (i.e., that should otherwise take place by a de-reconstruction of the diamond (100)-2 × 1 surface). Hence, the N-doped diamond (100) surface is 2 × 1-reconstructed (see Figure 9). In addition, both diamond (111) and (100)-2 × 1 surfaces show surface conductivities, which is induced by the clear evidence of spin densities within the O adsorbate layers (see Figures 9 and 10). Except for non-doped
diamond (100) surfaces, this was also the situation for all non-doping and doping situations in the present study.

Figure 9. Resulting geometrical structures after structural relaxation of N-doped O$_{\text{ontop}}$-terminated (a) (111) and (b) (100) surfaces. The carbon, hydrogen, oxygen, and nitrogen atoms are shown in grey, white, red, and blue, respectively. The calculated spin densities are also presented in the figure. The iso-surface value is 0.05 for both surface planes. The blue color shows the positive density, and the yellow color shows the negative density.

Like the situation with the BG values, the calculated valence band maxima (VBM) resulted in different numerical values for the two diamond surface planes. However, the results were very similar when comparing N-doped with P-doped diamond surfaces. As can be seen in Table 1, the order of $\Phi$ for the (111) surface became NH$_2$ < OH = H < O$_{\text{ontop}}$ < F for N-doping, and NH$_2$ < OH < H < O$_{\text{ontop}}$ < F for P-doping. These orders are almost identical, and of almost the same order when compared with the B-doped diamond (111) surface; NH$_2$ < H < OH < O$_{\text{ontop}}$ < F. Here, it is of a large interest to compare these $\Phi$ orders (i.e., for doped diamond) with the one obtained for non-doped diamond; NH$_2$ < OH < H < O$_{\text{ontop}}$ < F. It is thereby possible to draw the conclusion that substitutional doping by B, N, or P will not affect the order of work functions (at least not to any larger extent). Moreover, the corresponding values of $\Phi$ for N-doped (111) surfaces were 3.1, 4.6, 4.6, 5.4, and 5.9 eV. As can be seen in Table 1, these values are slightly larger than for B-doped diamond (111). Also, the corresponding values of $\Phi$ for P-doped (111) surfaces were 3.7, 4.8, 4.9, 5.4, and 6.1 eV. These are the values that are even larger than for N-doped diamond (111). A clear trend is thereby observed.

For the (100) surfaces, the $\Phi$ order is as follows: H = O$_{\text{bridge}}$ < NH$_2$ < OH < O$_{\text{ontop}}$ = F for N-doping, and H = O$_{\text{bridge}}$ < NH$_2$ < OH < O$_{\text{ontop}}$ < F for P-doping (see Table 2). These orders are also almost identical. However, the order of $\Phi$ values for B-doped diamond (100) surfaces is different; NH$_2$ < H < OH < O$_{\text{bridge}}$ < F < O$_{\text{ontop}}$. This is also the situation for a non-doped diamond surface; NH$_2$ < H
< O_{bridge} < F < OH < O_{ontop}. So it is again possible to state that the diamond (111) and (100) surface planes behave completely different with respect to electronic properties. Moreover, the corresponding values of $\Phi$ for the N-doped (100) surfaces were 3.7, 3.7, 3.8, 4.2, 5.3, and 5.3 eV. Also, the corresponding values of $\Phi$ for P-doped (100) surfaces were 4.0, 4.0, 4.1, 4.5, 5.3, and 5.5 eV. These values are thereby somewhat larger than for N-doped diamond (100), which in turn are, with one exception, somewhat larger than for B-doped diamond (100). As was the situation for diamond (111), one can also here see a clear trend.

![Partial Density of States](image)

**Figure 10.** Calculated DOS spectra for N-doped O_{ontop}-terminated (a) (111) and (b) (100) surfaces. The spectra cover the upper surface parts (i.e., O_{ontop}-terminating layer, dopant, and C atoms in the upper two atomic layers). The unit of the x-axis is eV, and the unit of the y-axis is electron density. The Fermi level is positioned at 0 eV. Blue—s-states; Orange—p-states.
As can be seen in Tables 1 and 2 and Figures S3, S4, S7, and S8, all variously terminated (111) and (100) surfaces display PEA values. In addition, there is no possibility to use visible light in photo-induced emission of electrons from either N- or P-doped diamond surface planes [(111) or (100)].

9. Summary and Conclusions

The combined effect of surface plane, termination, and doping, on the electronic structure of a diamond surface, has been studied in the present investigation by using theoretical DFT calculations. The bandgap values, work functions, electron affinities, as well as the probability for solar-induced photoemission of electrons, were of a special interest to study. The surface planes studied were (111) and (100). Moreover, the terminating species were H, F, OH, O_{ontop}, O_{bridge}, and NH\textsubscript{2}. In addition, the diamond surfaces were either non-doped, n-type doped (with N or P), or p-type doped (with B).

With few exceptions, the electronic structures for non-doped diamond (111) and (100) surfaces were found to be quite different. In fact, this was the situation for all three measures of electronic structures: bandgap (BG) values, work functions, and electron affinities (EAs). However, there were also some similarities. The BG values for the OH–, O_{ontop}, O_{bridge}, and NH\textsubscript{2}-terminating species were for both surface types apparently smaller than for the H- and F-terminated surfaces. More specifically, the DOS-calculations showed that the O_{ontop}-terminated (100) surface is electronic conducting. Furthermore, the H– and NH\textsubscript{2}-terminated (111) and (100) surfaces were found to have negative electron affinities (NEAs), while most of the other termination types resulted in positive electron affinities (PEAs). The OH-terminated (100) surface is an exception, which render a NEA value. Another dissimilarity worth mentioning is that it is possible to photo-induce electron emission (by solar light) from a NH\textsubscript{2}-terminated (111) surface, while this is not possible for the (100) counterpart (or for any of the other terminated surface types).

As was the situation with non-doped diamond surfaces, B-doped (111) and (100) also show completely different electronic structures. With one exception, it was found that B-doping will induce smaller BG values (i.e., as compared with non-doped diamond). Interestingly, there is no possibility for the B-doped diamond (111) and (100) surfaces to undertake photo-induced electron emission (by using visible light). B-doping was also found to induce smaller \(\Phi\) values, and to increase the electron affinities to more positive values. Exceptions are the EA value for the OH-terminated (111) surface, and for the F-terminated (100) surface, which showed a decrease in values. In short, B-doped H- and OH-terminated (111) surfaces, as well as B-doped H\textsubscript{2}, OH\textsubscript{2}, and NH\textsubscript{2}-terminated (100) surfaces, showed negative electron affinities (NEAs). In addition, a B-doped F-terminated (111) surface showed an EA value of zero, while the other terminating situations showed PEAs.

The effect by N-dopants was completely different in that the diamond (111) and (100) surfaces showed very similar electronic properties (there is only one exception, and that is the situation with NH\textsubscript{2}-terminated surfaces). On the contrary, doping with P elements rendered quite dissimilar electronic structures. As expected, the BG values for the P- or N-doped surfaces where much smaller as compared with non-doped diamond. Moreover, the calculated BG values for N-doped diamond surfaces were somewhat smaller as compared with the corresponding P-doped surfaces. As a test, similar calculations were performed for N-doped bulk diamond. It was then observed that the BG value for a substitutional positioned N dopant was considerably smaller than for a substitutional positioned N dopant with a vacant neighboring site (i.e., an NV-site). As was the situation with B-doped diamond surfaces, there is no possibility for the N or P-doped diamond (111) and (100) surfaces to undertake photo-induced electron emission (by using visible light).

N-doping was also found to induce larger \(\Phi\) values for the variously terminated (111) surface, and this was even more the situation for the corresponding P-doped surfaces. As expected, the EA values for both N- and P-doped surfaces [(111) and (100)] were found to be positive. When comparing the results of these two n-type dopant species, it was found that the EA values for H- and F-, termination were larger for the N-doping situations. The other terminating species (OH, O_{ontop}, O_{bridge}, and NH\textsubscript{2}) were found to induce larger EA values for the P-doped surface.
In summary, it has been shown in the present study that it is not only the type of doping that is of large importance for the electronic structure of a diamond surface. Both the type of surface plane and the type of surface termination are of large importance for the final surface electronic properties.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2311-5629/6/2/22/s1, Figure S1: Calculated DOS spectra for non-doped terminated (100) surfaces, Figure S2: Calculated DOS spectra for B-doped terminated (100) surfaces, Figure S3: Calculated DOS spectra for N-doped terminated (100) surfaces, Figure S4: Calculated DOS spectra for P-doped terminated (100) surfaces, Figure S5: Calculated DOS spectra for non-doped terminated (111) surfaces, Figure S6: Calculated DOS spectra for B-doped terminated (111) surfaces, Figure S7: Calculated DOS spectra for N-doped terminated (111) surfaces, Figure S8: Calculated DOS spectra for P-doped terminated (111) surfaces.

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**References**

1. Shenai, K.; Scott, R.S.; Baliga, B.J. Optimum semiconductors for high-power electronics. *Electron Devices IEEE Trans.* 1989, 36, 1811–1823. [CrossRef]
2. Ley, L.; Ristein, J.; Meier, F.; Riedel, M.; Strobel, P. Surface conductivity of the diamond: A novel transfer doping mechanism. *Physica B* 2006, 376–377, 262–267. [CrossRef]
3. Uppireddi, K.; Westover, T.; Fisher, T.; Weiner, B.R.; Morell, G. Thermionic emission energy distribution from nanocrystalline diamond films for direct thermal-electrical energy conversion applications. *J. Appl. Phys.* 2009, 106, 043716. [CrossRef]
4. Koeck, F.; Nemanich, R. Substrate-diamond interface consideration for enhanced thermionic electron emission from nitrogen doped diamond films. *J. Appl. Phys.* 2012, 112, 113717. [CrossRef]
5. Neugebohrn, N.; Sun, T.; Koeck, F.; Hembree, G.G.; Nemanich, R.J.; Schmidt, T.; Falta, J. Spatial correlation of photo-induced and thermionic electron emission from low work function diamond films. *Diam. Relat. Mater.* 2013, 40, 12–16. [CrossRef]
6. Suzuki, M.; Ono, T.; Sakuma, N.; Naoshi Sakai, T. Low-temperature thermionic emission from nitrogen-doped nanocrystalline diamond films on n-type Si grown by MPCVD. *Diam. Relat. Mater.* 2009, 18, 1274–1277. [CrossRef]
7. Sowers, A.T.; Ward, B.L.; English, S.L.; Nemanich, R.J. Field emission properties of nitrogen-doped diamond films. *J. Phys. D Appl. Phys.* 1999, 36, 3973–3982. [CrossRef]
8. Koeck, F.A.M.; Nemanich, R. Emission characterization from nitrogen-doped diamond with respect to energy conversion. *Diam. Relat. Mater.* 2006, 15, 217–220. [CrossRef]
9. Koeck, F.A.M.; Nemanich, R.J.; Balasubramaniam, Y.; Haenen, K.; Sharp, J. Enhanced thermionic energy conversion and thermionic emission from doped diamond films through methane exposure. *Diam. Relat. Mater.* 2011, 20, 1229–1233. [CrossRef]
10. Sherehiy, A.; Dumpala, S.; Sunkara, M.K.; Jasinski, J.B.; Cohn, R.W.; Sumanasekera, G.U. Thermionic emission from phosphorus (P) doped diamond nanocrystals supported by conical carbon nanotubes and ultraviolet photoelectron spectroscopy study of P-doped diamond films. *Diam. Relat. Mater.* 2014, 50, 66–76. [CrossRef]
11. Kono, S.; Takyo, G.; Amano, N.; Plusnin, N.I.; Mizuochi, K.; Aoyama, T.; Goto, T.; Abukawa, T.; Namba, A.; Tasumi, N.; et al. Mechanism of Field Emission from a Highly Phosphorous-Doped Chemical Vapor Deposition Diamond (111) Surface. *Ipn. J. Appl. Phys.* 2007, 46, L21–L24. [CrossRef]
12. Yamada, T.; Masuzawa, T.; Mimura, H.; Okano, K. Electron emission from conduction band of heavily phosphorous doped diamond negative affinity surface. *J. Phys. D Appl. Phys.* 2016, 49, 045102. [CrossRef]
13. Kato, H.; Takeuchi, D.; Ogura, M.; Yamada, T.; Kataoka, M.; Kimura, Y.; Sobue, S.; Nebel, C.E.; Yamasaki, S. Heavily phosphorus-doped nano-crystalline diamond electrode for thermionic emission application. *Diam. Relat. Mater.* 2016, 63, 165–168. [CrossRef]
14. Haque, A.; Narayan, J. Electron field emission from Q-carbon. *Diam. Relat. Mater.* 2018, 86, 71–78. [CrossRef]
15. Haque, A.; Narayan, J. Stability of electron field emission in Q-carbon. *MRS Commun.* 2018, 8, 1343–1351. [CrossRef]
16. Narayan, J.; Bhaumik, A.; Gupta, S.; Haque, A.; Sachan, R. Progress in Q-carbon and related materials with extraordinary properties. *Mater. Res. Lett.* 2018, 6, 353–364. [CrossRef]
17. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865–3868. [CrossRef]
18. Fischer, T.H.; Almlof, J. General methods for geometry and wave function optimization. *J. Phys. Chem.* 1992, 96, 9768. [CrossRef]
19. Clark, S.J.; Segall, M.D.; Pickard, C.J.; Hasnip, P.J.; Probert, M.I.J.; Payne, M.C. First principles methods using CASTEP. *Z. für Krist.* 2005, 220, 567–570. [CrossRef]
20. Hohenberg, P.; Kohn, W. Inhomogeneous electron gas. *Phys. Rev. B* 1964, 136, 864–871. [CrossRef]
21. Kohn, W.; Sham, L.J. Self-consistent equations including exchange and correlation effects. *Phys. Rev. A* 1965, 140, 1133–1138. [CrossRef]
22. Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B* 1990, 41, 7892–7895. [CrossRef] [PubMed]
23. Monkhorst, H.J.; Pack, J.D. Special points for Brillouin-zone integrations. *Phys. Rev. B* 1976, 13, 5188–5192. [CrossRef]
24. Parr, R.G.; Yang, W.T. Density functional-approach to the frontier-electron theory of chemical-reactivity. *J. Am. Chem. Soc.* 1984, 106, 4049–4050. [CrossRef]
25. Yang, W.; Parr, R.G.; Pucci, R. Electron-density, Kohn-Sham Frontier Orbitals, and Fukui Functions. *J. Chem. Phys.* 1984, 81, 2862–2863. [CrossRef]
26. Mulliken, R.S. Electronic population analysis on LCAO–MO molecular wave functions. 1. *J. Chem. Phys.* 1955, 23, 1833–1840. [CrossRef]
27. QuantumWise Atomistix ToolKit (ATK) with Virtual NanoLab, Version January 2018. Available online: https://www.synopsys.com/silicon/quantumatk.html (accessed on 1 January 2019).
28. Ferreira, L.G.; Marques, M.; Teles, L.K. Approximation to density functional theory for the calculation of band gaps of semiconductors. *Phys. Rev. B* 2008, 78, 125116. [CrossRef]
29. Delley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *J. Chem. Phys.* 1990, 92, 508–517. [CrossRef]
30. Delley, B. From molecules to solids with the DMo13 approach. *J. Chem. Phys.* 2000, 113, 7756–7764. [CrossRef]
31. Tian, Y.; Larsson, K. Theoretical studies of size effects on surface chemical properties for nanoscale diamond particles. *J. Phys. Chem. C* 2014, 118, 26061.
32. Larsson, K. *Novel Aspects of Diamond. The Effect of Dopants on Diamond Surface Properties and Growth*; Springer: Cham, Switzerland, 2017.
33. Zou, Y.; Larsson, F.; Larsson, K. Effect of CVD diamond growth by doping with nitrogen. *Theor. Chem. Accounts* 2014, 133, 1432.
34. Zou, Y.; Larsson, K. Effect of boron doping on the CVD growth rate of diamond. *J. Phys. Chem. C* 2016, 120, 10658. [CrossRef]
35. May, P.W.; Stone, J.C.; Ashfold, M.N.R.; Hallam, K.R.; Wang, W.N.; Fox, N.A. The effect of diamond surface termination species upon field emission properties. *Diam. Relat. Mater.* 1998, 7, 671–676. [CrossRef]
36. Mackey, B.L.; Russell, J.N., Jr.; Crowell, J.E.; Butler, J.E. Effect of surface termination on the electrical conductivity and broad-band internal infrared reflectance of a diamond (110) surface. *Phys. Rev. B* 1995, 52, R17009–R17012. [CrossRef]
37. Martin, H.B. Hydrogen and oxygen evolution on boron-doped diamond electrodes. *J. Electrochem. Soc.* 1996, 143, L133–L136. [CrossRef]
38. Nebel, C.E.; Erlt, F.; Sauerer, C.; Stutzmann, M.; Graeff, C.F.O.; Bergonzolo, P.; Williams, O.A.; Jackman, R.B. Low temperature properties of the p-type surface conductivity of diamond. *Diam. Relat. Mater.* 2002, 11, 351–354. [CrossRef]
39. de Theije, F.K.; Roy, O.; van der Laag, N.J.; van Enckevort, W.J.P. Oxidative etching of diamond. *Diam. Relat. Mater.* 2000, 9, 929–934. [CrossRef]
40. Wang, M.; Simon, N.; Decorse-Pascasun, C.; Bouttemy, M.; Etcheberry, A.; Li, M.; Boukherroub, R.; Szunerits, S. Comparison of the chemical composition of boron-doped diamond surfaces upon different oxidation processes. *Electrochim. Acta* 2009, 54, 5818–5824. [CrossRef]
41. Ferro, S.; De Battisti, A. The 5-V window of polarizability of fluorinated diamond electrodes in aqueous solutions. *Anal. Chem.* 2003, 75, 7040–7042. [CrossRef]

42. Kondo, T.; Ito, H.; Kusakabe, K.; Okhawa, K.; Einaga, Y.; Fujishima, A.; Kawai, T. Plasma etching treatment for surface modification of boron-doped diamond electrodes. *Electrochem. Acta.* 2007, 52, 3841–3848. [CrossRef]

43. Song, K.-S.; Degawa, M.; Nakamura, Y.; Kanazawa, H.; Umezawa, H.; Kawarada, H. Surface-modified diamond field-effect transistors for enzyme-immobilized biosensors. *Jpn. J. Appl. Phys.* 2004, 43, L814–L817. [CrossRef]

44. Bhattacharyya, S.; Auciello, O.; Birrell, J.; Carlisle, J.A.; Curtiss, L.A.; Goyette, A.N.; Gruen, D.M.; Krauss, A.R.; Schlueter, J.; Sumant, A.; et al. Synthesis and characterization of highly-conducting nitrogen-doped ultrananocrystalline diamond films. *Appl. Phys. Lett.* 2001, 79, 1441–1443. [CrossRef]

45. Frangi, G.; Jomard, F.; Pinault, M.A. Influence of tertiarybutylphosphine (TBP) addition on the CVD growth. *Diam. Relat. Mater.* 2005, 14, 355–363. [CrossRef]

46. Yu, B.D.; Miyamoto, Y.; Sugino, O. Efficiency of n-type doping of diamond using surfactant-mediated epitaxial growth. *Appl. Phys. Lett.* 2000, 76, 976–978. [CrossRef]

47. Haase, A.; Peters, A.; Rosiwal, S. Growth and thermoelectric properties of nitrogen-doped diamond/graphite. *Diam. Relat. Mater.* 2016, 63, 222–226. [CrossRef]

48. Haque, A.; Sumaiya, S. An overview on the formation and processing of nitrogen-vacancy photonic centers in diamond by ion implantation. *J. Manuf. Mater. Proc.* 2017, 1, 6. [CrossRef]

49. Koizumi, S.; Kamo, M.; Sato, Y.; Ozaki, H.; Iinuzuka, T. Growth and characterization of phosphorus-doped [111] homoepitaxial diamond thin films. *Appl. Phys. Lett.* 1997, 71, 1065–1067. [CrossRef]

50. Kato, H.; Yamasaki, S.; Okushi, H. Growth and characterization of phosphorus-doped diamond using organophosphorus gases. *Phys. Stat. Sol. (a)* 2005, 202, 2122–2128. [CrossRef]

51. Frangieh, G.; Jomard, F.; Pinault, M.A. Influence of tertiarybutylphosphine (TBP) addition on the CVD growth of diamond. *Phys. Stat. Sol. (a)* 2009, 206, 1996–1999. [CrossRef]

52. Koizumi, S.; Kamo, M.; Sato, Y.; Ozaki, H.; Inuzuka, T. Growth and characterization of phosphorus-doped [111] homoepitaxial diamond thin films. *Appl. Phys. Lett.* 1997, 71, 1065–1067. [CrossRef]

53. Ohta, N.; Yamamoto, T.; Jannssens, S.D. Large improvement of phosphorus incorporation efficiency in n-type chemical vapor deposition of diamond. *Appl. Phys. Lett.* 2014, 105, 232106. [CrossRef]

54. Matsumoto, T.; Kato, H.; Makino, T.; Ogura, M.; Takeuchi, D.; Okushi, H.; Yamasaki, S. Carrier transport in homoepitaxial diamond films with heavy phosphorus doping. *Jpn. J. Appl. Phys.* 2014, 53, 05FP05. [CrossRef]

55. Grotjohn, T.A.; Tran, D.T.; Yaran, M.K.; Demlow, S.N.; Schuelke, T. Heavy phosphorus doping by epitaxial growth on the (111) diamond surface. *Diam. Relat. Mater.* 2014, 44, 129–133. [CrossRef]

56. Hoshino, Y.; Hoshino, Y.; Kato, H.; Makino, T.; Ogura, M.; Iwasaki, T.; Hatano, M.; Yamasaki, S. Electrical properties of lateral p–n junction diodes fabricated by selective growth of n+ diamond. *Phys. Stat. Sol. (a)* 2012, 209, 1761–1764. [CrossRef]

57. Makino, T.; Yoshino, K.; Sakai, N.; Uchida, K.; Koizumi, S.; Kato, H.; Takeuchi, D.; Ogura, M.; Oyama, K.; Matsumoto, T.; et al. Enhancement in emission efficiency of diamond deep-ultraviolet light emitting diode. *Appl. Phys. Lett.* 2011, 99, 061110. [CrossRef]

58. Takeuchi, D.; Makino, T.; Kato, H.; Ogura, M.; Okushi, H.; Ohashi, H.; Yamasaki, S. High-voltage vacuum switch with a diamond p–i–n diode using negative electron affinity. *Jpn. J. Appl. Phys.* 2012, 51, 090113. [CrossRef]

59. Maier, F.; Ristein, J.; Ley, L. Electron affinity of plasma-hydrogenated and chemically oxidized diamond (100) surfaces. *Phys. Rev. B* 2001, 64, 165411. [CrossRef]

60. Touhara, H.; Okino, F. Property control of carbon materials by fluorination. *Carbon* 2000, 38, 241–267. [CrossRef]

61. Takeuchi, D.; Kato, H.; Ri, G.S.; Yamada, T.; Vinod, P.R.; Hwang, D.; Nebel, C.E.; Okushi, H.; Yamasaki, S. Direct observation of negative electron affinity in hydrogen-terminated diamond surfaces. *Appl. Phys. Lett.* 2005, 86, 152103. [CrossRef]

62. McCleery, R.L. Advanced carbon electrode materials for molecular electrochemistry. *Chem. Rev.* 2008, 108, 2646–2687. [CrossRef]

63. Pleskov, Y.V. Photoelectrochemical Properties of semiconductor diamond. *J. Electroanal. Chem.* 1987, 228, 19–27. [CrossRef]
64. Swain, G.; Ramesham, R. The electrochemical activity of boron-doped polycrystalline diamond thin-film electrodes. *Anal. Chem.* 1993, 65, 345–351. [CrossRef]

65. Williams, A.; Lightowl, E.; Collins, E. Impurity conduction in synthetic semiconducting diamond. *J. Phys. Part C Solid State Phys.* 1970, 3, 1727. [CrossRef]

66. Chrenko, R. Boron, dominant acceptor in semiconducting diamond. *Phys. Rev. B* 1973, 7, 4560–4567. [CrossRef]

67. Li, H.D. Investigation on crystalline structure, boron distribution, and residual stresses in freestanding boron-doped CVD diamond films. *J. Cryst. Growth* 2010, 312, 1986–1991. [CrossRef]

68. Butler, J.E.; Vikharev, A.; Gorbachev, A.; Lobaev, M.; Muchnikov, A.; Radischev, D.; Isaev, V.; Chernov, V.; Bogdanov, S.; Drozdov, M.; et al. Nanometrical diamond delta doping with boron. *Phys. Stat. Sol.* 2017, 11, 1600329–1600333.

69. Sakai, T.; Ono, T.; Sakuma, N.; Yoshida, H.; Suzuki, M.; Takeuchi, D.; Kono, S.; Yamasaki, S. Observation of negative electron affinity in low-voltage discharging boron-doped polycrystalline diamond. *Jpn. J. Appl. Phys.* 2014, 53, 05FP09. [CrossRef]

70. Müller-Sebert, W.; Wörner, E.; Fuchs, F.; Wild, C.; Koidl, P. Nitrogen induced increase of growth rate in chemical vapor deposition of diamond. *Appl. Phys. Lett.* 1996, 68, 759–760. [CrossRef]

71. Liu, T.; Raabe, D. Influence of nitrogen doping on growth rate and texture evolution of chemical vapor deposition diamond films. *Appl. Phys. Lett.* 2009, 94, 211191–211193. [CrossRef]

72. Dunst, S.; Sternschulte, H.; Schreck, M. Growth rate enhancement by nitrogen in diamond chemical vapor deposition—A catalytic effect. *Appl. Phys. Lett.* 2009, 94, 224101–224103. [CrossRef]

73. Bohr, S.; Haubner, R.; Lux, B. Influence of phosphorus addition on diamond CVD. *Diam. Relat. Mater.* 1995, 4, 133–144. [CrossRef]

74. Kalish, R. The search for donors in diamond. *Diam. Relat. Mater.* 2001, 10, 1749–1755. [CrossRef]

75. Kajihara, S.A.; Antonelli, A.; Bernholc, J.; Car, R. Nitrogen and potential n-type dopants in diamond. *Phys. Rev. Lett.* 1991, 66, 21101. [CrossRef]

76. Jiang, N.; Hatta, A.; Ito, T. Nitrogen Doping Effects on Electrical Properties of Diamond Films. *Jpn. J. Appl. Phys.* 1998, 37, L1175–L1177. [CrossRef]

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