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Simulation of Diamond Surface Chemistry: Reactivity and Properties

Karin Larsson

Abstract

The diamond material possesses very attractive properties, such as superior electronic properties (when doped), in addition to a controllable surface termination. During the process of diamond synthesis, the resulting chemical properties will depend not only on the adsorbed species but also on the type of substitutional doping element. The combination of adsorbate and dopant will thus have the ability to influence both the chemical and electronic properties of a diamond surface. All resulting (and interesting) properties of doped and terminated diamond surfaces make it clear that these types of material modifications are very important for a variety of applications that are based on photoactivated chemical processes. Theoretical modeling has been shown to act as an important scientific tool in explaining and predicting experimental results. Simulation of the dependence of, e.g. surface termination and doping on diamond material properties, is expected to give important information about various surface electronic properties (like photo-induced surface electrochemistry).

Keywords: diamond, doping, theory, electronic properties

1. Introduction

The diamond material possesses very attractive properties, such as high transparency, high thermal conductivity at room temperature, radiation hardness, as well as an extreme mechanical hardness. It is also chemically inert. In addition, diamond also exhibits superior electronic properties (including high carrier mobility), large electrochemical potential window, low dielectric constant, controllable surface termination, and a high breakdown voltage [1]. However, the large band gap (5.4 eV) limits the usage of diamond for electronic devices. Hence, impurities have been introduced into the diamond lattice in order to eliminate this limitation. Impurities within a diamond lattice can dramatically change both the geometrical and electronic properties.

More generally, the properties of a surface (for solid material) depend on various factors, such as (i) number of binding atoms (i.e. for the atoms in the diamond surface plane), (ii) surface reconstructing, (iii) type and degree of chemisorption to the surface, and (iv) elemental doping within the upper surface region. The number of binding atoms to a surface atom (i) is always smaller than for a bulk atom, making it more reactive (since it has the driving force to become bulk-like).

This is also the underlying reason to the specific surface electronic properties, which differ from the corresponding bulk scenario. Moreover, factors (ii)–(iv) do all represent changes in the surrounding electron density for the surface atoms, of which all are different from the situations with bulk atoms.

The boron atom is one of the most commonly used p-type dopants. The B-doped diamond electrode is a semiconducting material with very promising properties like (i) a wider potential window in aqueous solution (approximately -1.35 to $+2.3$ V vs. the normal hydrogen electrode), (ii) low background current, and (iii) corrosion stability in aggressive environments [2]. 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 [3–6]. 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, phosphorus has instead been introduced as a plausible n-type donor in diamond (111) [7]. Phosphorus, P, is nowadays the only well-established substitutional n-type donor [8]. Kato et al. produced this type of n-type diamond epilayer on (100)-oriented diamond surfaces [9]. N-type diamond heavily doped with P atoms has more recently been obtained with low electric resistivity and low incorporation activation energy [10, 11]. This makes phosphorus-doped diamond more promising for device applications, e.g. as an electron source for bipolar devices [12–14], as Schottky barrier diodes [15], and for thermionic emission applications [16].

Surface termination is the general notation when a surface-binding species is used to uphold the cubic structure or to change the surface properties of diamond. For instance, hydrogen-terminated B-doped diamond surfaces have been found to be hydrophobic [17]. An H-terminated P-doped diamond surface has also been found to show negative electron affinity (NEA) [18]. (NEA means that electrons in the conduction band of diamond easily emit from the surface.) Electron emission from the conduction band of H-terminated P-doped homoepitaxial diamond (111) has experimentally been observed [16, 19]. The oxygen atom is also one of the most commonly used diamond surface-terminating species. Oxygen-terminated diamond surfaces do generally show hydrophilic properties [20], as well as a positive electron affinity. 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 [21]. Fluorine-termination will, compared to H-termination, result in an even more hydrophobic diamond surfaces. 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 [22, 23]. 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 [24].

All these interesting properties of terminated diamond surfaces make it clear that surface termination is crucial for especially those applications for which diamond can function as an electrode material. The relative stability and the electronic structures of the variously doped diamond surfaces, terminated with either H, O-containing groups, F or NH_2 , are therefore very important to study from an atomic-level point of view.

Theoretical modeling, using density functional theory (DFT), has been shown to be a valuable tool in the explanation and prediction of experimental results. For instance, DFT calculations have been shown powerful in studying thin film growth mechanisms, as well as for the simulation of surface reconstruction, modification, and functionalization, respectively.

2. Methods and methodologies

Theoretical modeling has been found useful in the (i) interpretation of experimental results and in the (ii) prediction of parameters in the design of experimental setups. First-principle DFT calculations have thereby become useful for a variety of materials of practical importance. This method is, however, quite demanding since it relies on the electrons in the systems under investigations. Hence, this circumstance puts a strong demand in the model size. It should here be stressed that these more advanced computational methods are needed when studying chemical reactions, where bonds are formed and/or broken. Other observables that are very sensitive to the theoretical method used, with its parameters, are the electronic structures with their intrinsic band gaps. In conclusion, first-principle DFT methods are very useful for studies of, e.g. electronic and geometrical surface structures, in addition to surface reactivity and chemical processes.

Periodic boundary conditions are most frequently used for DFT calculations on solid surfaces or interfaces. For this purpose, an ultrasoft pseudopotential [25] plane-wave approach is most often used, which, in turn, is based on the Perdew-Wang (PW91) generalized gradient approximation (GGA) [26] for the exchange-correlation functional. The GGA method takes into account the gradient of the electron density, which improves the accuracy of, e.g. the bond energies [27].

The model used under periodic boundary conditions are the so-called super cells where these cells will become translated in x-, y-, and z-directions, forming an infinite three-dimensional model. In the case of modeling surfaces, only a part of the supercell will be filled (i.e. in x- and y-directions), forming a repetitive pattern of infinite slabs with a vacuum layer in between. This vacuum layer has to be large enough to avoid any type of interactions between neighboring slabs.

3. Surface reactivities

There are two factors that are very important for a solid surface reactivity. One is the number of binding atoms for a surface atom. The other factor is the density of surface atoms. Bulk diamond C atoms bind covalently, with sp^3 hybridized bonds, to four C neighbors in. For the most commonly observed diamond facets (111) and (100), the (111) surface atoms only have three binding neighbors, whilst the corresponding (100) atoms have two (**Figure 1a, c**). (These surfaces are then assumed to be non-reconstructed.) When instead describing the situation in terms of dangling bonds (i.e. unpaired electrons), a (111) surface atom has only one dangling bond. On the other hand, the (100) surface has two dangling bonds, which makes it more reactive (as compared with the (111) surface). However, the presence of dangling bonds is most often the cause of a high surface reactivity. Hence, surface reconstructions may occur, with a resulting lowering of the surface energy. This is the reason why an ideal diamond (100) surface (i.e. (100)- 1×1) most often undertakes a surface reconstruction, thereby forming a (100)- 2×1 surface structure (**Figure 1d**). As a matter of fact, also the more ideal (111) surface (i.e. (111)- 1×1) will at higher temperatures be transferred to a 2×1 reconstruction (i.e. (111)- 2×1), called the Pandey chain structure (**Figure 1b**).

The relative energies for these surface structures have earlier been calculated theoretically by using an ab initio DFT method [28]. It was then shown that the 2×1 -reconstruction of the bare diamond (100) surface will result in a stabilization of the total energy by 1.85 eV per surface C. The corresponding energy stabilization for the bare diamond (111) surface was found to be 0.54 eV per surface C

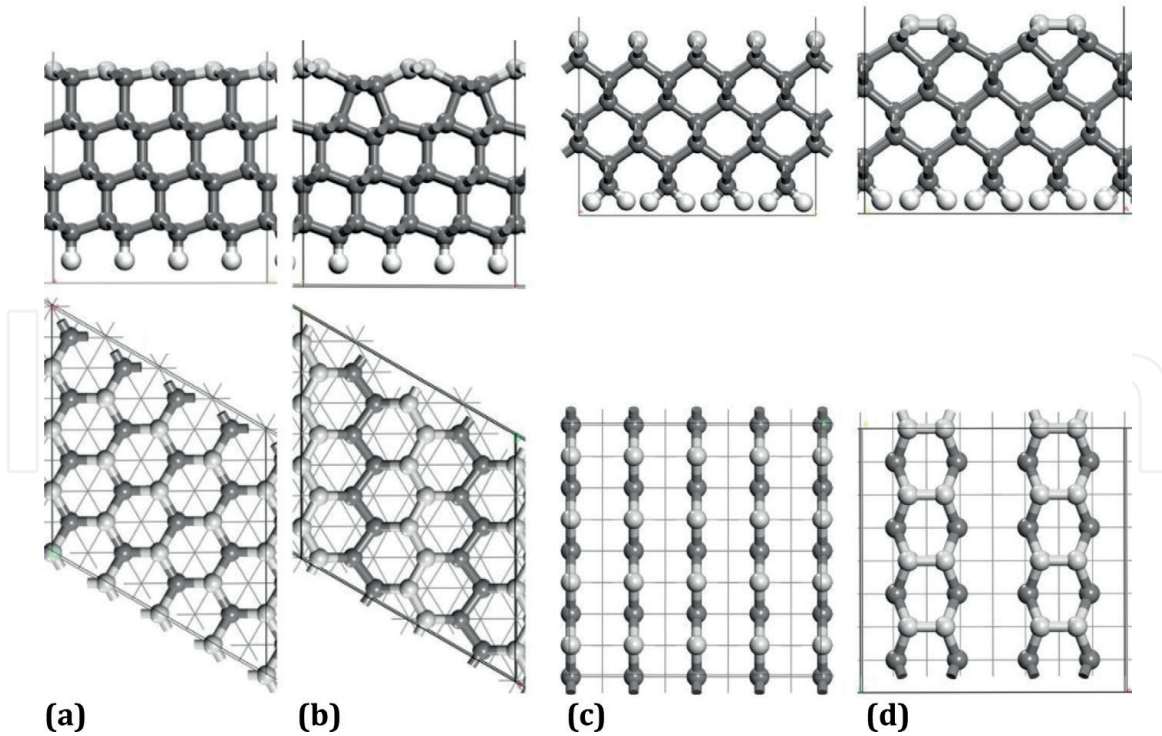


Figure 1. Optimized periodic models of diamond (111)-1 × 1 (a), (111)-2 × 1 (b), (100)-1 × 1 (c), and (100)-2 × 1 (d) surfaces. The upper row shows a side view of the different models, and the lower row shows on-top orientations. The top-most C atoms are shown with a whiter shade.

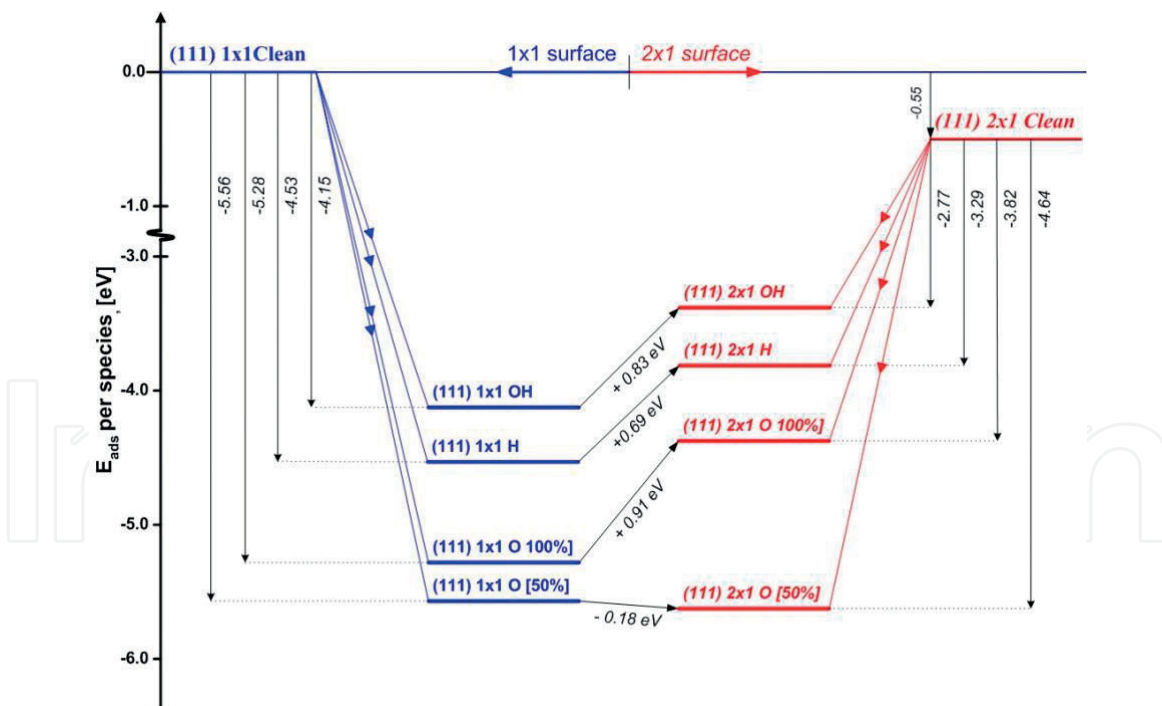


Figure 2. Adsorption energies for various terminating species (H, OH, and O) onto (1 × 1)- and (2 × 1)-reconstructed diamond (100) and (111) surfaces.

(see **Figure 2**). These stabilization energies do not give any information about the possibility for a transfer from, e.g. a non-reconstructed diamond (100) surface to a 2 × 1-reconstructed (100) surface (i.e. the kinetics of a phase transformation). However, the activation energy (i.e. energy barrier) for this specific phase transformation was earlier studied by performing DFT calculations. A very small energy barrier of energy (0.32 eV) was obtained for the phase transformation from the

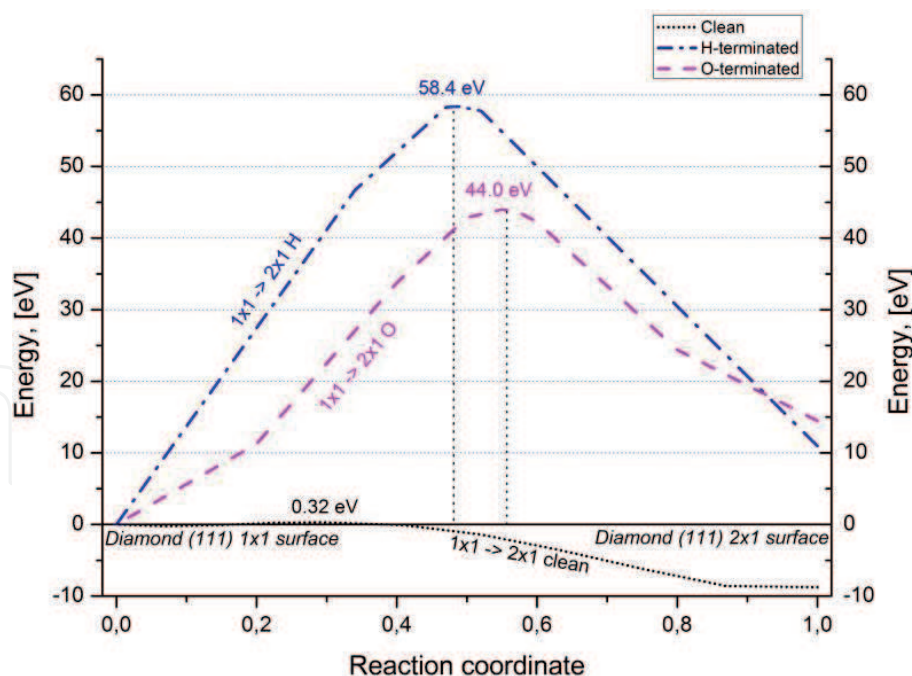


Figure 3. Calculated activation energies for transformation between diamond (111), (1 × 1), and (2 × 1) structures as a function of surface termination with H and O, respectively.

non-reconstructed (111) surface to the slightly more stable 2 × 1-reconstruction of the same surface (also called a Pandey-Chain structure) (**Figure 3**). This minor barrier energy was recently justified by using ab initio molecular dynamic (MD) simulations on a non-reconstructed diamond (111) at 500 K [29].

4. Energetic stability of surface termination

4.1 General

The adsorption of various species onto diamond (111) and (100) surfaces were theoretically studied in earlier studies by the present author [28, 30]. The adsorption energies for the species O and OH are presented in **Figures 4** and **5**, where the adsorption and stabilization energies are shown over the whole range (0–100%) of surface coverage. Each of these figures starts with a 100% surface coverage with H adsorbates. These H adsorbates are then, one by one, replaced with oxygen atoms or hydroxyl molecules.

The stabilization energies in these figures are defined as the total adsorption for a 100% coverage of H, O, or OH, to be compared with the total adsorption energy for a 100% H-terminated diamond surface. A negative stabilization energy does, hence, mean that the corresponding surface configuration is energetically more favorable than a completely H-terminated surface.

4.2 Hydrogen termination

A clean surface was the starting point for the hydrogen adsorption studies. As was shown in Ref. 28, the clean (111)-2 × 1 surface is energetically more favorable than the corresponding 1 × 1 reconstruction (**Figure 6**). However, the (111)-1 × 1 phase becomes favorable for a hydrogen coverage above 30%. It has also experimentally been shown that a small number of hydrogen atoms on the diamond surface will reconstruct the (111)-2 × 1 to the 1 × 1 configuration [30]. A LEED pattern showed

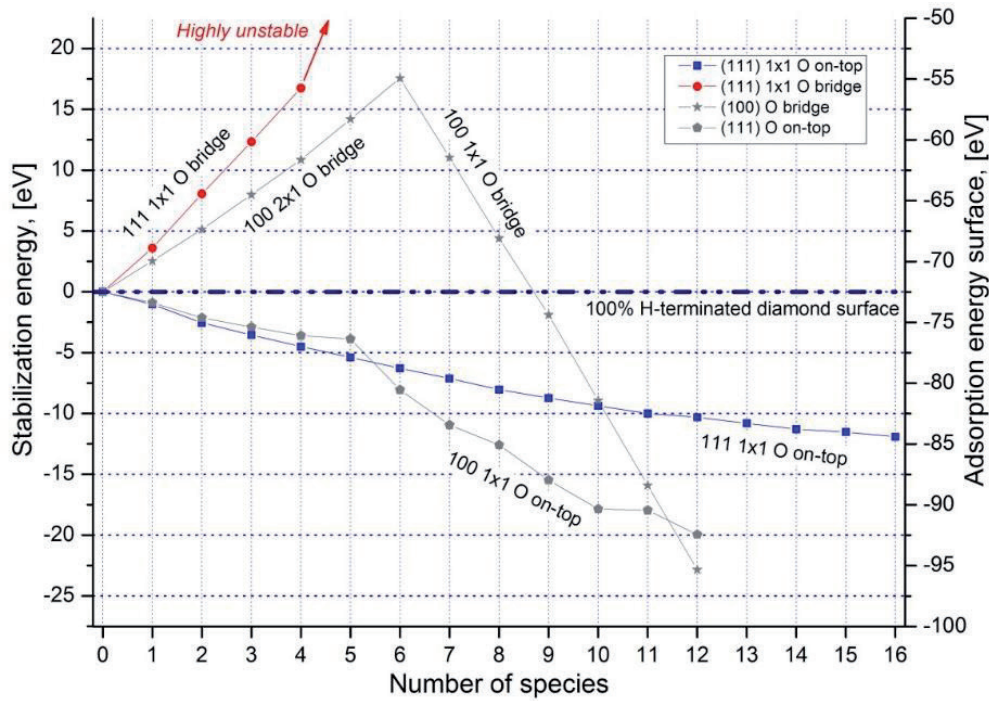


Figure 4. An initially 100% H-terminated diamond (100)-2 × 1 or (111)-1 × 1 surface is successively oxygen-terminated by successively replacing the H adsorbates with O in either bridge or on-top positions.

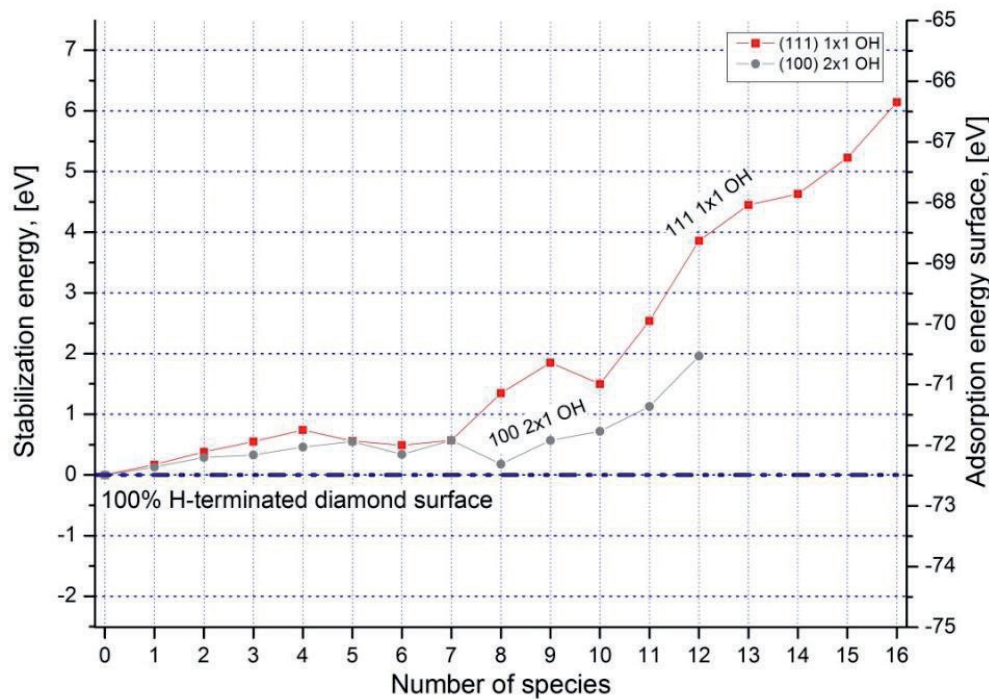


Figure 5. Stabilization and adsorption energies for a successively replacement of H adsorbates with OH groups on diamond (100)-2 × 1 and (111)-1 × 1 surfaces.

that 0.05 ML would effectively reconstruct the (111)-2 × 1 surface to the 1 × 1 reconstruction. Hence, hydrogen atoms are not able to stabilize the Pandey chain carbon atoms as much as they do for the non-reconstructed 1 × 1 surface. A plausible explanation may be that the delocalized π -bonds of the Pandey chain are weakened. Hence, the electron configuration that stabilized the clean Pandey chain becomes perturbed.

The value of the adsorption energy for hydrogen on the diamond (100)-1 × 1 surface was in Ref. [30] found to be surprisingly large (-6.96 eV). Two hydrogens

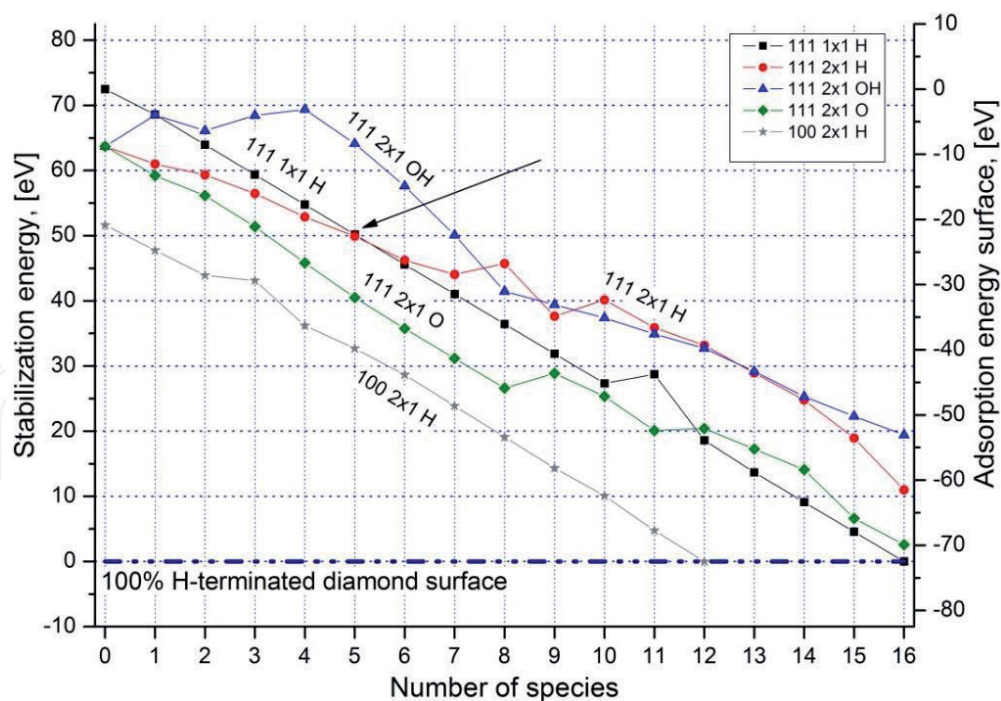


Figure 6. A non-terminated 2×1 reconstructed diamond (111) surface successively H-, O-, and OH-terminated with increments of one adsorbate. A comparison with H-termination on diamond (111)- 1×1 and (100)- 2×1 is here included. The arrow identifies the H-coverage here; a (111)- 1×1 and a (111)- 2×1 surface have identical stabilization energy.

per carbon atom were chemisorbed onto the surface in order to saturate the two dangling bonds (per surface carbon) and thereby to uphold the sp^3 configuration and prevent 2×1 reconstruction. This dihydride configuration has been under much speculation [31–35], but it is generally accepted [36] that it does not occur during CVD growth conditions. The very favorable adsorption energy for the dihydride surface configuration is probably not seen experimentally due to the favorable (and spontaneous) 2×1 reconstruction. Moreover, the calculated adsorption energy for hydrogen on the 2×1 -reconstructed (100) surface (-4.30 eV [30]) is in excellent agreement with experimental investigations [37].

In summary, the most stable H-terminated diamond surfaces phases under experimental conditions are pristine (111) and 2×1 -reconstructed (100) (**Figure 6**).

4.3 Oxygen termination

Oxygen atoms are generally more effective than hydrogen in stabilizing a diamond surface. This is most probably due to the divalent nature of oxygen, whereby it may break C-C double bonds and form two C-O bonds. As a consequence, a high surface coverage of oxygen will yield a de-reconstruction of the 2×1 -reconstruction of the diamond (100) surface into a bulk-equivalent 1×1 surface structure. This is shown in **Figure 4** for the termination with O atoms in both on-top and bridge positions [30]. As presented in Ref. 30, the most favorable position for oxygen on the (100) surface seems to be the bridge position which is supported by other experimental and theoretical studies [38–40]. The spontaneous reconstruction from (100)- 2×1 to (100)- 1×1 is shown in **Figure 4**. This implies that no activation barrier is present during this specific surface phase transformation process (since DFT is a 0 K method).

For the situation with a diamond (111) surface, no surface de-reconstruction was observed as a result of oxygen adsorption (100% coverage) onto the (111)- 2×1 surface. Hence, the (111)- 2×1 to (111)- 1×1 reconstruction must be associated with

an activation energy. This is true for also the reverse direction. Furthermore, the on-top and bridge positions of O were only found stable for an oxygen coverage less than 50% (for both diamond (111)- 2×1 and 1×1).

In summary, the most stable O-termination of a diamond (100) surface seems to take place for oxygen in bridge position on the bulk-like (100)- 1×1 surface. For the situation with a diamond (111) surface, the most stable O-termination is most probably for an on-top position at a surface coverage of 100%.

4.4 Hydroxyl-termination

For the terminating OH groups, there are two types of adsorbate-adsorbate interactions: hydrogen bonding (energy stabilization) and steric repulsions (energy destabilization). The hydrogen bonding will be noticeable at lower OH coverage, whereas steric repulsion dominates at higher coverage. The destabilization of OH-terminated surfaces is supported by an experimental study that reports a small number of hydroxyl groups present on an oxygenated (100) surface [1]. Hydrogen-bonding enthalpies of -0.15 eV were thereby reported.

The adsorption of OH groups onto diamond surfaces was calculated in Ref. 30, using a DFT method. The results for a 2×1 -reconstructed (100) were found to be -4.1 eV. Hence, this adsorption energy is in good agreement with the corresponding results for the 1×1 surface: -4.2 eV (0.1 eV difference). Another DFT study for the diamond (111) surface has reported almost identical results for the OH adsorption energies of -4.2 (-4.0) eV for the 1×1 (and 2×1) reconstruction.

As shown in Ref. 28, the theoretically calculated adsorption energies for OH groups adsorbed onto the Pandey chain are unfavorable up to a 30% surface coverage (see **Figure 5**). A severe weakening of the π -bond chain, as well as absence of hydrogen bonding, is probably responsible for this effect.

4.5 Fluorine-termination

The adsorption of fluorine onto diamond (100) and (111) surfaces in their most common surface reconstructions (1×1 and 2×1) was also studied in Refs. 28 and 30. Only 100% terminated surfaces were considered. Fluorine is the termination species that most resembles hydrogen: monovalent with a rather small covalent radius. Fluorine was found to be strongly adsorbed to all of the studied diamond surfaces (-5.53 , -6.33 , -4.56 , and -4.56 eV for the (100)- 1×1 , (100)- 2×1 , (111)- 1×1 , and (111)- 2×1 surfaces, respectively). Although the diamond (100)- 1×1 surface has two unpaired electrons, two fluorine atoms per carbon (difluoride configuration) atom was in Ref. 30 found to be highly unstable.

5. Effect by terminating species on the diamond surface electronic structure

The diamond surface electron structure and properties, such as electron affinity (EA) and work function (WF), have earlier been studied both experimentally and theoretically in a vast number of publications. The diamond surfaces included both (111) and (100) surface planes, and the dominant surface-terminating species were hydrogen (H), oxygen, as well as fluorine. A mixture of O-containing species is most probably present on the surface, and it is not yet outlined how the atomic-level structure looks like for fluorinated surfaces. However, what is missing is a more detailed information about the influence of N-containing adsorbates on both the (111) and (100) diamond surfaces. This is also the situation for, theoretically,

the extreme situation with a 100% coverage of O_{ontop} , O_{bridge} , OH, F or NH_2 , species. The aim with a recent study by the present author was, hence, to theoretically investigate the effect by these individual terminating species on especially the EA of diamond (111) and the 2×1 -reconstructed (100) surface. This theoretical study was based on DFT calculations, and the results are presented in **Table 1**.

At first, the DFT method used in calculating the electronic structures was evaluated by comparing the calculated band gap for bulk diamond with the experimental one: 5.4 vs. 5.5 eV. These band gaps were found to be almost identical, and, hence, the present DFT method was chosen for all of the density of state (DOS) calculations in the present study.

As a result of the geometry optimizations, it was not possible to bind O in bridge position on the diamond (111) surface. These O atoms were in the course of the optimization immediately transferred to on-top positions instead. Moreover, the (111) surface stayed in this state, and did not reconstruct to the Pandey Chain reconstruction when being adsorbed to. This was also the situation for the 2×1 -reconstructed (100) surface and for all terminating situations except for O_{ontop} adsorption. This specific adsorption induced a re-reconstruction to diamond (100)- 1×1 . The reason for this process is that O forms a double bond with the surface carbon, thereby breaking the C-C bond within the paired C couple on the reconstructed (100) surface.

As can be seen in **Table 1**, the adsorption of H, OH, and NH_2 resulted in negative electron affinities (NEA) for both diamond (111) and (100); -1.0 , -0.4 , and -2.0 eV for diamond (111); and -0.7 , -1.3 , and -0.9 eV for diamond (100). For comparison, the experimentally obtained value of NEA for H is about -1.1 . Hence, the here presented calculation of EA for H adsorption shows a very good resemblance with experimental findings. Moreover, adsorption of F, O_{ontop} , and O_{bridge} resulted in positive electron affinities (PEA): $+1.1$ (F) eV for diamond (111) and $+2.1$, $+3.8$, and $+0.4$ eV for diamond (100). Also, O_{ontop} adsorption onto diamond (111) resulted in a metallic surface (i.e. surface electron conductivity). For comparison, the experimentally obtained value of PEA for oxygen is about $+1.7$. Hence, the here presented calculation of EAs for oxygen adsorption shows a not so good resemblance with experimental findings. But it must here be stressed that there is most probably a mixture of O-species on the surface, and it is not possible to analyze (experimentally) this distribution more in detail.

eV	H	OH	F	O_{ontop}	O_{bridge}	NH_2
(111)						
VBE	-4.0	-4.0	-5.8	Cond.	---	-2.3
EA	-1.0	-0.4	+1.1	Cond.	---	-2.0
(100)						
VBE	-4.8	-3.9	-7.0	-4.3	-4.4	-3.4
EA	-0.7	-1.3	+2.1	+3.8	+0.4	-0.9

The values are given in eV.

Table 1.
 Positions of the valence band edge (VBE) and value of electron affinity (EA) for variously terminated diamond (111) and (100) surfaces.

6. Effect by doping on the diamond surface electronic structure

6.1 General

Diamond, as a material, possesses quite unique electrochemical properties, such as a large electrochemical potential window, a low dielectric constant, controllable surface termination, and a high breakdown voltage [41]. However, the large band gap (5.4 eV) limits the usage of diamond for electronic devices. Hence, impurities have been introduced into the diamond lattice, which can dramatically change both the geometrical and electronic properties. The boron atom is one of the most commonly used p-type dopants. It has been found that the B dopant will increase the electronic conductivity, as compared with the intrinsic non-doped diamond [1]. For different doping levels, the diamond material will show a metallic-type conductivity [42, 43], p-type semi-conductivity [44, 45], and superconductivity [46]. Nitrogen and phosphorus are commonly used as n-type dopants within the diamond material. However, substitutional doping with N atoms creates a deep donor level in diamond, which limits the usage of this material as an n-type semiconductor [3–6]. Instead, substitutional doping with phosphorus is regarded to be more efficient in creating an n-type semiconductor [7, 47].

6.2 Substitutional B doping

Substitutional doping with boron atoms did not render any major structural changes in the diamond surface region, as compared to the corresponding non-doped situations. Moreover, the atomic dopant was positioned within the second C layer, and this was the situation for all three different types of dopants studied (i.e. B, N, and P). The reason to this position is that these dopants have earlier been found to have a major influence on the surface structure and properties when positioned in C layer 2.

As can be seen in **Table 1**, the adsorption of H, OH, and NH₂ resulted in NEAs for B-doped diamond (111): -0.6 , -0.3 , and -0.6 eV. It was, however, only H-terminated diamond (100) surfaces that resulted in a NEA of -0.6 . The other terminating species (OH and NH₂) resulted in PEAs of $+0.1$ and $+3.2$ eV. The results obtained for the (111) surface are thus similar to the non-doped situation, whilst it is completely different for the (100) surface.

As can further be seen in **Table 1**, the adsorption of F species on both the (111) and (100) B-doped diamond surfaces resulted in PEA values of $+0.8$ vs. $+1.1$ eV. Moreover, the influence by B doping was found to be very small. As stated above, adsorption of O in bridge position was only feasible for the diamond (100) surface. The calculated PEA value for the B-doped surfaces was $+0.7$ eV, which is also very similar to the corresponding value for a non-doped surface. On the contrary, the calculated results for O_{ontop} position were completely different when comparing diamond (111) with (100). Both non- and B-doped (111) surfaces rendered surface conductivity (i.e. a metallic-like situation), whilst the PEA values obtained for the (100) surfaces were completely different with respect to each other: $+3.8$ (non-doped) vs. $+1.1$ (B-doped) eV. An experimentally obtained EA value for the oxygen-terminated non-doped diamond surface is about $+1.7$ eV. However, it should be kept in mind that a surface coverage with oxygen most often involves a variety of O-related species (e.g. O and OH), as well as different types of adsorption sites (e.g. O_{ontop} and O_{bridge}). It is therefore very difficult to compare experimental values with theoretically obtained ones.

6.3 Substitutional N doping

As was the situation with B doping, substitutional doping with nitrogen atoms within the second diamond C layer did not render any major structural changes in the diamond surface region, as compared to the corresponding non-doped situations.

As can be seen in **Table 1**, the adsorption of H, OH, and NH₂ resulted in NEAs for N-doped diamond (111): -0.5 , -0.1 , and -0.8 eV. On the contrary, these species resulted in an electrically conductive surface for diamond (100). Hence, the valence bands were not filled when using these terminating species in combination with substitutional N doping. Moreover, the other terminating species (O_{ontop} and F) on the diamond (111) species resulted also in an electrically conductive surface. The results obtained for the (111) surface are thus, with one exception, similar to the non- (or B-) doped situation. F-termination on a non- (or B-) doped diamond (111) surface resulted in a PEA, whilst it gave surface conductivity for the corresponding N-doped situation.

When comparing diamond (111) with (100) in **Table 1**, it is obvious that only O_{ontop}-termination yielded similar results for the two different surface planes (i.e. surface electronic conductivity). The other surface-terminating species gave completely different results. For O_{bridge}-termination on diamond (100), which cannot be found on diamond (111), it was shown that O_{bridge}-termination in combination with B doping will render a PEA value of $+2.6$ eV. This value is closer to the experimental value for non-doped diamond (100) ($+1.6$ eV) than to the calculated one ($+0.4$ eV). When comparing an N-doped diamond (100) surface with non- (or B-) doped counterparts, it has been found that only O_{bridge}- and F-termination will give similar results (i.e. PEA values). The other terminating species (H, OH, O_{ontop}, and NH₂) give completely different results.

6.4 Substitutional P doping

As was the situation with both B and N doping, substitutional doping with phosphorus atoms within the second diamond C layer did not render any major structural changes in the diamond surface region, as compared to the corresponding non-doped situations.

As can be seen in **Table 1**, the adsorption of all adsorbates (H, F, O_{ontop}, O_{bridge}, OH, and NH₂) resulted in electrically conductive surfaces for diamond (111). On the contrary, almost all of these species resulted in PEAs for diamond (100): $+0.5$ (H), $+2.2$ (F), $+3.9$ (O_{ontop}), $+3.0$ (O_{bridge}), and $+0.8$ (OH) eV. The only adsorbate that did not render a PEA value was NH₂, which instead resulted in a NEA value (-0.7 eV). The results obtained for the (111) surface are thus, with only one exception, completely different compared to the non-, B-, or N-doped situation. O_{ontop}-termination gave surface electronic conductivities for both non-doped and doped diamond (111) surfaces. F-termination resulted in surface conductivity for both P- and N-doped diamond (111), whilst non- and B-doped surfaces showed PEA values. Moreover, H, OH, and NH₂ adsorbates induced NEA values, which is completely different to the surface conductivity observed for P-doped diamond (111).

Surface-terminated P-doped diamond (100) surfaces gave results that were both similar and dissimilar to the other types of doping situations. F- and O_{bridge}-termination gave PEA values for all non-doped and doped situations (B, N, and P). O_{ontop}-termination resulted in PEA values for non-, B-, and P-doped surfaces, whilst it for N-doped diamond gave surface conductivity. As can be seen in **Table 1**, H-, OH-, and NH₂-termination resulted in a mixture of all three types of surface electronic properties (i.e. surface conductivity, PEA, and NEA), depending on the type of doping situation.

7. Conclusions

The combined effect of surface termination and substitutional doping on diamond surface electronic properties has here been presented and discussed. Firstly, the stability and geometrical structures of variously terminated diamond (111) and (100) surfaces were presented. The terminating species included H, F, OH, O_{ontop}, O_{bridge}, and NH₂. Moreover, the results for the doped surfaces were compared with non-doped diamond (111) and (100) surfaces. The doping species included B, N, and P. Theoretical DFT calculations had been used for the here presented results.

As a result of these first-principle calculations, F- and O_{bridge}-terminations gave PEA values for all non-doped and doped situations. Moreover, O_{ontop}-termination resulted in PEA values for non-, B-, and P-doped surfaces, whilst it for N-doped diamond gave surface conductivity. Various results were obtained for the other combinations of surface terminations and doping situations.

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