

Hydrogen and Fluorine Adsorption on the h-BN (001) Plane

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The adsorption of H or F species on B vs N atoms on the h-BN (001) surface has been investigated theoretically within the DFT method, using a cluster approach. Only the boron atoms were subjected to a local transformation from hexagonal to cubic phase. It occurred either upon the adsorption of F species or the adsorption of H species. For the latter situation, a neighboring surface B atom was substituted by a C atom and, hence, the number of electrons in the system was increased. The nitrogen atoms did not undergo, with one exception, any phase transformation. The adsorption of H species resulted in a local transformation from sp^2 to sp^3 hybridization with a hereby connected negative adsorption energy (-55 kJ/mol). This adsorption process is therefore highly unlikely to occur in a CVD synthesis.

Introduction

Cubic boron nitride (c-BN) exhibits interesting and outstanding properties. Its extreme hardness, large band gap, high thermal conductivity, and transparency make it a suitable material for mechanical, optical, thermal, and electronic applications.^{1–3} Furthermore, it possesses a high thermal stability both in oxidizing environments and in contact with Fe, Co, and Ni.⁴ It is therefore promising as a tool coating for machining of steel, cast iron, and ferrous alloys. It can also be made as both n- and p-type semiconductors, suitable for p-n junction diodes.¹

Cubic BN can be manufactured using high pressure and high temperature methods (HPHT). However, production of c-BN by various thin film techniques suffers from several problems. Physical vapor deposition (PVD) techniques yield only very thin single-phase c-BN, and always with an interlayer of amorphous and hexagonal BN at the substrate–coating interface. This leads to poor adhesion of the films.^{5–10} Using chemical vapor deposition (CVD) techniques, the films become a multiphase mixture of h-BN and amorphous/turbostratic BN.^{4,10,11}

Since hexagonal BN is one of the products when using any of the PVD or CVD methods, we will in the present work investigate the possibility to, under certain experimental conditions, use h-BN as a provider for nucleation sites (i.e., as a substrate for c-BN growth). In this case, further growth of h-BN will decrease. In diamond CVD, graphite has been investigated both experimentally^{12–14} and theoretically¹⁵ as a provider of sites for nucleation and growth. Both hot-filament¹² and microwave plasma assisted^{13,14} CVD experiments show that the nucleation of diamond takes place preferentially on the prism plane $\{hk*0\}$ surface¹⁶ and not on the basal plane (001) surface of highly oriented pyrolytic graphite (HOPG). The Hartree–Fock (HF) study of energetics found a preferential nucleation of diamond in favor of a continuous growth of graphite on the (100) and (110) edges of the graphite (001) plane.¹⁵ Similar theoretical studies have also been performed for h-BN acting as a substrate in diamond growth.^{17,18} They show the same result, i.e., that diamond growth is energetically more stable than the corresponding growth of graphite nuclei on the h-BN (001) edges.

Hot-filament experiments confirm the usefulness of h-BN as substrate in diamond-CVD, however, without specifying whether the nucleation occurs on the basal plane or on the edges of h-BN (001).¹⁹ No theoretical investigations have so far been made for c-BN nucleation on h-BN. Neither on the different $\{hk*0\}$ edges nor on the (001) plane.

The purpose with the present work is to make a structural and energetic investigation of induced c-BN nucleation sites on the (001) plane of h-BN, assuming a condition of supersaturation of either H or F in the gaseous phase. The H or F species are then thought to adsorb on either B or N surface atoms in the h-BN plane. These two species have earlier been shown to be effective as terminating species on c-BN (111) cluster surfaces.²⁰ If the surface atoms are adapting the sp^3 hybridization configuration, the adsorbing surface atom (and its adsorbed species) may be regarded as an embryo of a c-BN nucleus. According to the definition of nuclei, a c-BN nucleus would consist of three atoms or more. The “embryonic nucleus” will therefore require further adsorption and reaction with B- (or N-) containing species to become a real nucleus. Unless otherwise stated, nuclei mentioned onward in the text will refer to this single atom (or atoms) in the h-BN plane that has attained the cubic “phase” (sp^3 configuration) from the corresponding hexagonal one upon adsorption of H or F, respectively.

Boron nitride, being isoelectronic with the carbon polymorphs, can be doped with carbon to produce electron-rich or -deficient surfaces. If a C atom substitutes a B atom, being situated very close to the surface, the number of electrons near the surface will be increased. Correspondingly, the number of electrons near the surface will decrease as a result of a substitution of a N atom (close to the surface) with C. Hence, the effect of substitutional carbon impurities on the adsorption process of H vs F is also of a great interest to study.

Methods

The adsorption of H or F on the two types of surface atoms (B or N) of the hexagonal BN basal plane (001) surface was investigated within the framework of density functional theory

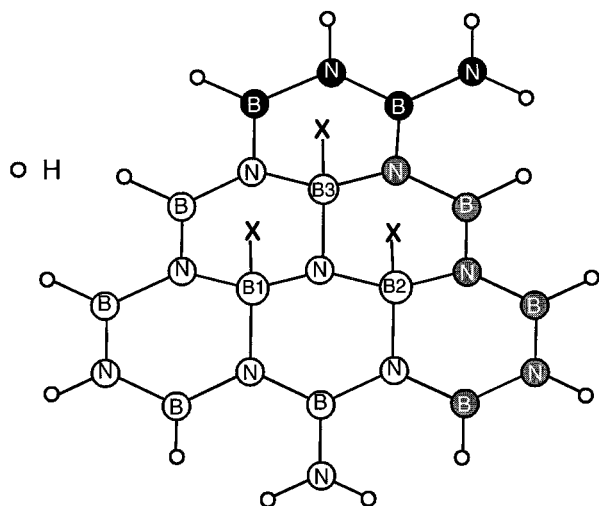


Figure 1. A model representing the h-BN (001)-B clusters. The geometry is also valid for the h-BN (001)-N surfaces. The B atoms are then replaced by N atoms, and vice versa. The white atoms represent a cluster with one adsorption site (B1). By adding the grayish and black atoms, a second (B2) and third (B3) adsorption site will be included in the cluster modeling the h-BN (001) surface.

(DFT),^{21,22} using the program system DMol²³ and a cluster approach. The total energies for both reactants and products of the adsorption process



where T^* is modeling the different h-BN (001) surfaces and X^* is H or F were calculated employing the following formula:

$$E_{\text{ads},X} = E_X + E_T - E_{T-X} \quad (2)$$

E_X , E_T , and E_{T-X} are the total energies for the different adsorbates and for the templates T , with and without an adsorbed species X , respectively.

A necessary condition for obtaining a good description of the electronic state of the reactants and products in the adsorption reaction [1] is to choose a highly flexible basis set and a model cluster adequately describing the h-BN surface and to use treatments which include electron correlation. In addition, geometry optimization is of great importance. A double numeric basis set with polarization functions (dnp) was used. The dnp basis set is comparable in quality to the commonly used Gaussian analytical basis set, 6-31G**.²⁴ This basis set is most suitable for polar compounds such as BN since it is improved, compared to the minimal basis set, in the description of expansions and contractions of the valence shell in response to different molecular environments. It also adequately describes charge rearrangements around the atoms.³²

A previous study of diamond nucleation on h-BN showed that clusters of the size $B_5N_5H_6$ and $B_7N_7H_8$ were sufficient in modeling nucleation on the (100) edge vs (110) edge of the (001) plane of h-BN.¹⁷ The investigation of the influence of electronegative substituents close to the nucleation site, however, required a slightly larger template ($B_9N_9H_{10}$).¹⁸ Three different cluster sizes will be used in the present investigation. The smallest one ($B_7N_7H_{10}X$ ($X = H$ or F)) contains one single adsorption site (B1). This cluster can be described as three B_3N_3 rings fused together and terminated with hydrogen atoms (Figure 1). As was found in the theoretical investigation by Carbone et al.,¹⁸ the electrons of the B_3N_3 ring system are delocalized over the three rings, which indicates that, all of the B and N atoms are sp^2 hybridized. Because of the difference in electronegativity,

there is, however, a higher electron density around the N atoms. By increasing the number of fused rings in the cluster (from three to five), a medium sized cluster ($B_{10}N_{10}H_{14}X_2$) will be formed, including also a second adsorption site (B2). The third cluster ($B_{12}N_{12}H_{17}X_3$) used in the present investigation contains three adsorption sites (B1, B2, and B3) in a BN system built up from six fused rings. When modeling the h-BN (001) surface, only the adsorbed species and the adsorbate-bonding surface atom(s) were allowed to fully relax. All other atoms were kept in fixed positions in order to hold the characteristics of the crystal. The bond length (r_{B-N}) chosen in the present investigation is the experimental value (1.446 Å).²⁵

The local density approximation (LDA),²² being one of the earliest approximations in DFT, includes correction for correlation effects. In DMol, the form for the exchange-correlation energy of the uniform electron gas is that derived by von Barth and Hedin.²⁶ However, one of the most important deficiencies with the LDA exchange, the incorrect asymptotic behavior, leads numerically to an overestimated chemical bond energy for the system. Using nonlocal functionals can solve this. As an example, there is the Becke (B88)²⁷ gradient-corrected exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr²⁸ (notated B-LYP). Bond lengths and angles, as well as bonding energies, are improved using B-LYP.^{29,30}

DMol uses numerical basis sets,²⁴ thus the various integrals arising from the expression for the energy equation need to be evaluated over a grid. The integration points of the grid are generated in terms of angular functions and spherical harmonics. The quality of the calculations depends on the selection of the set of integration points.³¹ Also the number of integration points of the grid used to generate the basis sets is of importance. All of the calculations in the present investigation were performed using the medium-sized grid. This grid provides a reasonable compromise between numerical precision and computational effort. However, as a systematic comparison, the fine grid was also used. The fine-meshed integration grid is computationally more costly but on the other hand more efficient in locating geometries representing more shallow energy minima on the potential energy surface.²⁴

Results and Discussion

A. General. Konyashin et al.¹⁰ have suggested that surface layer sp^2 -hybridized boron nitride can undergo a hybridization transformation to sp^3 -hybridized boron nitride after irradiation of the surface by hydrogen atoms. As discussed in the section Introduction, the assumed process of formation for embryonic c-BN nucleation on the basal plane of h-BN is, in the present investigation, thought to occur via adsorption of either H or F species. The main role of the adsorbates is then to transform the surface atoms from a hexagonal to a cubic phase. In order for the B (or N) atoms to undergo this phase transformation, the delocalized " π -bond" system must be ruptured locally and a σ bond must form between a substrate atom and an adsorbate atom. Three various clusters modeling the h-BN (001) surface are demonstrated in Figure 1. The smallest ($B_7N_7H_{10}X$), medium-sized ($B_{10}N_{10}H_{14}X_2$), and largest ($B_{12}N_{12}H_{17}X_3$) contain one, two, and three adsorption sites, respectively ($X = H$ or F). The medium-sized and largest clusters are predominantly used to investigate the effect of C substitution further from the observed adsorption site. The annotation h-BN (001)-B (or -N) corresponds to surface atom (B or N) that takes part in the adsorption process. Substrate-adsorbate interatomic distances $B-X$ and surface angles ν_{NBN} are presented in Tables 1 and 2.

TABLE 1: Average Interatomic Distances (B–X) and Average Angles ν_{NBN} for the h-BN (001)-B Surface Atoms with an Adsorbed Species X (X = H or F)

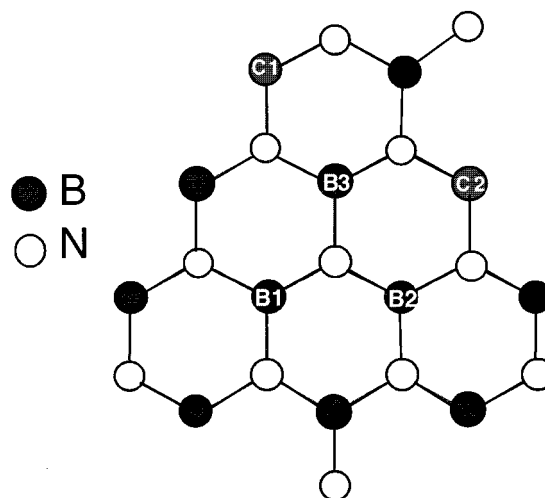
property	one adsorbed atom	two adsorbed atoms	three adsorbed atoms
B–H distance (Å)	3.40	3.20 (medium grid) 1.42 (fine grid)	3.30 (medium grid) 1.55 (fine grid)
angle ν_{NBN} (°)	120.0	118.1	118.3
B–F distance (Å)	1.45	1.44	1.45
angle ν_{NBN} (°)	111.9	111.1	111.5

TABLE 2: Average Interatomic Distances (B–H) and Average Angles ν_{NBN} for the h-BN (001)-B Surface Atoms with an Adsorbed Species H (One Nonadsorbing Boron Atom is Substituted with a C Atom in Different Positions)

property	closest to the adsorbing B atom	between adsorbing B atoms	furthest away from the adsorbing B atom
B–H distance (Å)	1.26	1.30	1.60
angle ν_{NBN} (°)	110.3	113.9	118.5

B. Surface Boron Atoms. (i) *Hydrogen Adsorption.* A medium-sized integration grid has been used in the present calculations. However, as a systematic test, a finer grid has also been employed. The structural geometry obtained when using the fine-meshed grid may either (i) represent a local minimum on the potential energy surface which differs from the minimum obtained by the medium-sized grid or (ii) the geometries may coincide and, hence, both types of grids represents the same minimum. Results obtained using both types of grid sizes will be presented only for those situations where a discrepancy in location of minima have occurred.

Adsorption of H species on the h-BN (001)-B plane does not lead to any localized transformation from “hexagonal” to “cubic” phase for the adsorbing B atoms in that the angles ν_{NBN} are 118–120° regardless of the template size. This implies almost total sp^2 hybridization for the adsorbing B atoms. This result is strongly correlated with the extremely small adsorption energy of 5 kJ/mol, calculated for the adsorption of one H to the smallest cluster demonstrated in Figure 1. By assuming that an increase in temperature is equivalent to an increase in the average kinetic energy of the adsorbed species, an increase in temperature of about 1000 °C (suitable for chemical vapor deposition of c-BN thin films) would result in an abstraction of the chemisorbed H species from h-BN (001)-B. This adsorption process is, hence, unlikely to occur at higher temperatures. The interatomic B–H distances show more variety, though. The B–H bond lengths on the singly and doubly adsorbed templates are 3.40 and 3.20 Å, respectively. In the latter case the two H atoms have dimerized (the H–H distance is 0.77 Å) at a distance from the surface of 3.18 and 3.21 Å, respectively. On the triply adsorbed template, two of the H atoms dimerize (H–H bond distance is 0.77 Å) at 4.7–4.3 Å from the BN-plane, while the third is located at a distance of 3.33 Å from the plane. However, the results obtained when performing geometry optimization with the fine integration grid in the 2-H and 3-H cases show a tendency for sp^3 hybridization for the B atoms. The average angles ν_{NBN} are 118.1° (118.3°) with a B–H average distance of 1.42 (1.55) Å. The data for the three-H case are in parentheses. These results represent a shallower minimum on the potential energy surface. The total energies for the 2-H and 3-H cases are less negative with 479 vs 358 kJ/mol compared to the more global-minimum geometries obtained when using the medium-sized grid. This strongly indicates an even less probability for an adsorption (negative adsorption energy) to occur. Hence, both medium- and fine-sized grids will

**Figure 2.** The model is representing the h-BN (001)-B cluster. For clarity, the terminating H atoms are not included. C1 is a carbon atom that is substituting a B atom in a position referred to as “closest” to B3 and “furthest away” from B1. C2 is situated in the position referred to as “between” B2 and B3.

result in a nonexistent possibility for adsorption of H to occur to the h-BN (001)-B type of surface.

However, interesting effects are observed when introducing electrons into the system. This is done by the substitution of B atoms with C atoms in different positions. The introduced electron(s) are found to have a significant impact on the hybridization state of the adsorbing B atom(s). A substitution has been made for B atoms in three significantly different positions: closest to, between, and furthest away from adsorbing B atoms (Figure 2). The position closest to the adsorbing B atom(s) is in the next neighboring position as a result of the BN network of alternating B and N atoms. “Between atoms” indicates a common position of joint B_3N_3 rings, where two or three adsorbing B atoms are sharing one C atom. The position “furthest away” is referring to a position in the adjacent B_3N_3 ring, relative to the ring containing the adsorbing B atom(s). The introduced electron(s) have a significant impact on the adsorbing B atom(s). First, the adsorption energy increases to 144 kJ/mol (compared to 5 kJ/mol for the undoped BN surface). Second, a strong correlation is observed between the position of the C atom and the degree of sp^3 hybridization for the adsorbing B atom (Table 2). The extra electron seems to be “absorbed” by the B atom in the B_3N_3 ring system, resulting in a transformation from sp^2 to sp^3 hybridization. The electron absorption effect is local, though. The closer the C atom is to the adsorbing B atom, the more sp^3 hybridization character it adapts. With the C atom in the position closest to the adsorbing B atom, the hybridization state of the B atom is completely sp^3 (ν_{NBN} being 110.3°). The angles gradually increase to 118.5° when the C atom is placed in the adjacent B_3N_3 ring (furthest away). This local effect was also observed in an LMTO-ASA-ES calculation of the electronic structure of c-BN by Zhang et al.³³ They stated that the impurity carbon would predominantly affect the density of states of its neighboring atoms.

The substitution of a B atom in the closest position also results in an increase of the adsorption energy for the H species. The extra electron hereby introduced in the system thus seems to provoke an increase in electron density between the surface B atom and the adsorbate, increasing the B–H bond strength by 139 kJ/mol.

When substituting an N atom with a C atom, a subtraction of electrons from the system will be the result. By doing so in

the position closest to the adsorbing B atom (the true neighboring position), the angle ν_{NBC} will become 119.8° . As a result of the geometry optimization, the H atom will then move from the B surface atom to a position right above the introduced C atom (C–H distance = 1.16 \AA). However, the C atom does not assume sp^3 hybridization (the angle ν_{BCB} is 120.0°). On the other hand, the H species has energetically been found to be rather strongly bonded to this specific surface site. The adsorption energy of H species (being attributed to the C–H bond) on this electron deficient type of surface is calculated to become 336 kJ/mol .

Guided by the results above, it is concluded that the sp^3 character of the adsorbing B atom is in decreasing order from the electron-rich to the electron-deficient surface. The boron atoms in h-BN (001) are thus strongly dependent on extra electrons in order to attain the cubic structure. Fewer electrons even prevent the B atoms to take any part in the adsorption process.

(ii) *Fluorine Adsorption.* The adsorption of fluorine is more undeviating than the hydrogen adsorption. The adsorbing surface B atoms will, as a result of the adsorption process, become mainly sp^3 hybridized (the average of ν_{BNB} is 111.5°). For the largest cluster modeling the h-BN (001) plane (Figure 1), the three adsorbed F atoms are, as a result of the geometry optimization, leaning somewhat outward from the center. Hence, they are experiencing strong electron–electron repulsion from each other and, thus, suffer from sterical hindrances. The closest F–F distance (3.15 \AA) is to be compared with the closest B–B distance (2.70 \AA). Furthermore, the F species terminating the surface B atoms will result in the largest adsorption energy (313 kJ/mol) obtained for a nondoped h-BN (001) surface in the present investigation. Hence, embryos of c-BN nuclei are possible to be formed on the h-BN (001) plane, using F as terminating species, both from an energetic as well as from a geometric point of view. The strong B–F bond will most probably be due to an ionic-covalent resonance bond strengthening (i.e., either a double bond between two ions (B^+ and F^-) or a single bond between B and F atoms).³⁴

Very minor geometrical changes were observed when introducing (or subtracting) electrons to the system, regardless of the position of the substituted atom. However, for the adsorption energy this was not the case. When increasing the number of electrons by substituting a B atom in the closest position with a C atom, the adsorption energy for F increased by almost 130 kJ/mol (to 441 kJ/mol). On the other hand, when decreasing the number of electrons by a corresponding substitution with N, the adsorption energy for F decreased by 98 kJ/mol (to 215 kJ/mol). Hence, it is also for F species concluded that the B atoms in h-BN (001) are strongly dependent on extra electrons in order to attain the cubic structure when bonded to the terminating species (here F).

C. Surface Nitrogen Atoms. (i) *Hydrogen Adsorption.* The geometry of the h-BN (001)-N surface can be seen in Figure 1. The model is actually representing the h-BN (001)-B surface, but the geometry is valid for the h-BN (001)-N surface as well with B atoms replaced by N atoms, and vice versa. As described in the section Methods, a model cluster is built up from one adsorption site until it contains three adsorption sites (N1, N2, and N3 in Figure 1). The interatomic distances N–X and angles ν_{BNB} are presented in Tables 4 and 5.

In contrast to the adsorption of hydrogen on the h-BN (001)-B surface, H adsorption onto the nitrogen atoms led to the formation of embryonic c-BN nuclei. No differences in geometry were found for any of the three cluster sizes (one, two, and

TABLE 3: Adsorption Energies in kJ/mol for the Two Species H and F on Different h-BN (001) Surface Atoms (B or N)

surface	H	F
1: h-BN (001)-B	5	313
1: with neighboring B substituted with C	144	441
1: with neighboring N substituted with C	336	215
2: h-BN (001)-N	–55	110
2: with neighboring B substituted with C	–63	344
2: with neighboring N substituted with C	55	138

TABLE 4: Average Interatomic Distances (N–X) and Average Angles ν_{BNB} for the h-BN (001)-N Surface Atoms with an Adsorbed Species X (X = H or F)

property	one adsorbed atom	two adsorbed atoms	three adsorbed atoms
N–H distance (\AA)	1.10	1.19	1.13
angle ν_{BNB} ($^\circ$)	111.0	112.0	110.6
N–F distance (\AA)	2.17	2.16	2.18
angle ν_{BNB} ($^\circ$)	120.0	119.9	119.9

TABLE 5: Average Interatomic Distances (N–F) and Average Angles ν_{BNB} for the h-BN (001)-N Surface Atoms with an Adsorbed Species F (Boron atom(s) are Substituted with Carbon in Different Positions)

property	closest to the adsorbing N atom	between adsorbing N atoms	furthest away from adsorbing N atom
N–F distance (\AA)	2.24	2.25	2.46
angle ν_{BNB} ($^\circ$)	118.2	119.9	118.3

three adsorbed H atoms, respectively). The average angle ν_{BNB} for all the three template sizes is 111.2° . This is rather close to the tetrahedral angle (109.5°), and the N atoms are thus subjected to a local phase transformation from a sp^2 (h-BN) to an almost complete sp^3 hybridized state (c-BN). However, the adsorption energy (Table 3) for an H species on a surface N atom is unfortunately negative (-55 kJ/mol). Albeit the geometrical results were promising, the adsorption energy (being the most important indicator for adsorption possibilities) tells us that it is impossible with H adsorption on the h-BN (001)-N surface in reality.

When investigating the effect of carbon impurities in the h-BN (001)-N surface, minor changes are observed. When introducing an electron into the B_3N_3 ring of the smallest cluster (containing one adsorption site), a decrease in the angle ν_{BNB} is observed (from 111.0° to 109.3°) but the N–H interatomic distance remains unchanged (1.10 \AA). Furthermore, the introduction of an extra electron to the system will decrease the N–H bond strength by 8 kJ/mol (to -63 kJ/mol). Hence, the possibility for hydrogen adsorption to surface nitrogen atoms is even smaller compared to the nondoped h-BN (001)-N surface (-55 vs -63 kJ/mol). When substituting a N atom with a C atom, and hereby subtracting an electron from the B_3N_3 ring system, the N–H bond distance contracts to 1.06 \AA and the angle ν_{BNB} increases to 114.6° . The adsorbing N atom thus shows a partial transition from sp^3 to sp^2 hybridization state. However, the decrease in number of electrons leads to an increase in adsorption energy for the H species. The N–H bond strength (adsorption energy) has become 55 kJ/mol , which is an increase by 110 kJ/mol compared to the undoped surface. The effect on adsorption energy is thus numerically very similar for electron introduction to the h-BN (001)-B surface and for electron subtraction from the h-BN (001)-N surface (139 vs 110 kJ/mol).

(ii) *Fluorine Adsorption.* The results of the adsorption of fluorine on the N surface sites are in contrast to the corresponding results of the adsorption on the equivalent B surface sites.

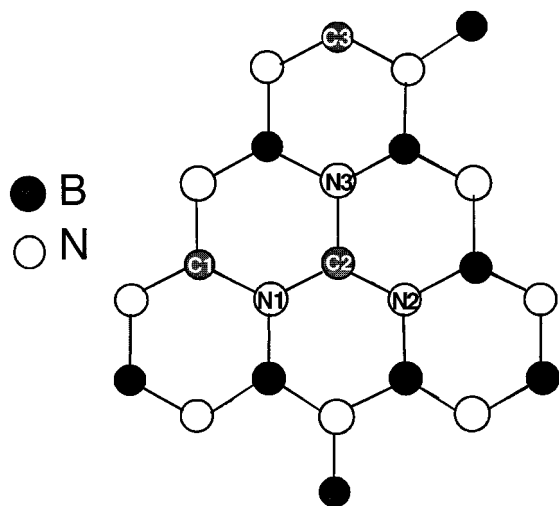


Figure 3. This model is representing the h-BN (001)-N cluster (without hydrogen atoms). C1 is a carbon atom, substituting a B atom, in a position referred to as “closest” to N1. C2 is in the position “between” N1, N2, and N3. C3 is “furthest away” from N3.

No indication of c-BN embryonic nucleus formation is observed for the adsorbing N atoms regardless of integration grid and cluster size. All angles ν_{BNB} are 119.9° , and consequently the N atoms remain in their sp^2 hybridization state. Even though the electron distribution is uniform over the B_3N_3 rings, the electronegativity difference between B and N implies a partial charge transfer from the boron to the nitrogen atoms.^{18,35} The gaseous fluorine atoms therefore experience a stronger electron repulsion when approaching the N surface atoms than they do approaching the B surface atoms. The F atoms are therefore somewhat repelled. The measured N–F bond length of 2.17 \AA for the clusters, compared to the N–F bond length of 1.36 \AA ³⁶ for NF_3 , illustrates this. The N–F interaction is thus not strong enough to evoke a phase transformation for the N atoms. The adsorption energy (being a measure of the bond strength) has been calculated to 110 kJ/mol . This is the highest adsorption energy obtained for the N atoms on the nondoped h-BN surface in the present investigation.

When electrons are introduced to the h-BN (001)-N surface, by substituting boron atoms in different positions with carbon atoms (Figure 3), the N–F bond distance is slightly elongated (from 2.17 \AA to $2.24\text{--}2.46 \text{ \AA}$). The shorter bond distance corresponds to the case when a B atom is replaced “closest to” and the longer bond distance corresponds to the replacement position “furthest away from” the adsorption site (Table 5). In addition, the angle ν_{BNB} is slightly decreased without any correlation to substitution position (average values of 119.9 to 118.8°). The adsorption energy for the F species on the h-BN (001)-N site increases by 234 kJ/mol (to 344 kJ/mol) upon the electron introduction. However, the high adsorption energy is attributed not to the N–F bond but to the B–F bond. During the geometry optimization, the F atom has moved from the originally bonding N atom to an energetically more favorable position, a neighboring B atom. This is on the analogy of the case with an electron-deficient boron surface. An adsorbed hydrogen atom was then found to migrate from the bonding B to a neighboring C atom, whereby the adsorption energy increased by 331 kJ/mol .

The fluorine-adsorbed h-BN (001)-N surface was also subjected to electron subtraction (by substituting an N atom with a C atom in different positions). The different substituting positions are equivalent to C1 and C2 in Figure 2. However, it should be emphasized that boron and nitrogen have changed

places so that B1, B2, and B3 now become N1, N2, and N3, respectively. Regardless of substitution position, the geometry of the surface remains identical to the nondoped h-BN surface. However, the electron subtraction slightly increases the adsorption energy by 28 kJ/mol (from 110 kJ/mol to 138 kJ/mol).

Judged by the adsorption energy, the nitrogen atoms are less likely to participate in the formation of embryonic c-BN nuclei, whether the (001)-N surface is nondoped, electron-rich or electron-deficient.

Conclusion

The adsorption of hydrogen or fluorine to the h-BN (001) basal plane has been investigated structurally and energetically, using the DFT method and a cluster approach. The h-BN model was either a nondoped h-BN (001) surface or a surface subjected to carbon impurities.

In what way the h-BN surface atoms will represent a small embryonic c-BN nucleus upon adsorption is guided both by geometrical and energetic considerations. The latter are most important in predicting the usefulness of different adsorbates in, e.g., various chemical vapor thin film depositions.

Geometrically, for the nondoped h-BN surface only the adsorption of fluorine on the B surface atoms, and the adsorption of hydrogen on the N surface atoms, will lead to the formation of small embryonic c-BN nuclei. The surface angles ν_{NBN} and ν_{BNB} indicate that the adsorbing surface atoms have been locally transformed from sp^2 to almost complete sp^3 hybridization state. However, the adsorption energies connected to these two types of bonds (B–F and N–H) are 313 and -55 kJ/mol , respectively. Conclusively, only the fluorine species are able to provoke the formation of an embryonic c-BN nucleus.

Transformation to sp^3 hybridization was observed for the H-adsorbed surface B atoms when introducing electrons into the h-BN (001) surface by substituting a B atom with a C atom. However, the effect of this extra electron is local, and for the full effect to occur the substitutional carbon atom must be adjacent to the adsorbing B atom. On the other hand, when subtracting an electron from the system (by substitution of an N atom with a C atom) the H atom is preferentially bonded to the neighboring C surface atom instead of the originally adsorbing B atom. The H adsorbed N surface atoms are geometrically more or less left unaltered, although the adsorption energy is increased when the BN surface is electron poorer.

To summarize the effects of altering the number of electrons on the surface, the surface boron atoms are positively affected upon an increase and negatively affected upon a decrease. The negative affection can even lead to migration of the hydrogen adsorbates away from the B atoms. The nitrogen surface atoms are not as sensitive, but too high an electron density may provoke migration of the fluorine species (from N to B adsorption sites).

The following conclusions can be drawn. At temperatures suitable for CVD processes ($600\text{--}1000^\circ\text{C}$), all adsorption energies but three are sufficient for adsorption to occur. The three exceptions are the nondoped B surface, the nondoped N surface, and the electron-deficient N surface, all hydrogen adsorbed. Among the possible adsorption processes, nucleation of c-BN is expected to occur on the F-adsorbed, nondoped B surface atoms. Second, embryonic cubic nuclei are possible to be formed on an H-adsorbed, electron-rich h-BN (001)-B surface. Finally, in the presence of surface carbon impurities on the electron-deficient B surface, the adsorption of H on these C impurities will yield an embryonic cubic nucleus.

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