

Surface Processes in Cubic Boron Nitride Growth: A Theoretical Study

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Various surface processes for the system B/N/H/F occurring during CVD growth of c-BN (111) have been investigated theoretically, using quantum mechanical methods. Both F and H species were found to be efficient as surface stabilizing agents. Mainly the H-terminated part of the B(111) surface will most probably undergo abstraction reactions, resulting in monoradical surface sites. The strongest adsorptions were found to occur on these newly created vacancies on the H-terminated part of the surface. This was especially the situation for the adsorption of NH_2 . The smallest probability for adsorption occurred on the F-terminated part of the surface. This was especially true for the adsorption of NF_2 . The surface mobility of NH_2 on the B(111) surface of c-BN was found to be much smaller compared to the mobility of CH_2 on diamond (111).

Introduction

Thin films of various materials play an important role in materials sciences today. Techniques to produce films with artificial structures, i.e., with desired combinations and distributions of the phases, are being developed. These structures include multiphase single layers, multilayers, superlattices, and clusters as well as laterally separated structures. However, there may be large difficulties in the fabrication of the different types of materials. For instance, there are often problems with heteroepitaxial growth of one material on another type of material. To obtain defect-free films, with good adhesion to the underlying material, is also not easy.

Different types of thin film techniques have been used in trying to deposit c-BN. They include chemical vapor deposition (CVD) and physical vapor deposition (PVD). Ion bombardments, with no hydrogen present in the gas phase, is being used within PVD. No ion bombardments, but instead a supersaturation of H, is being used within CVD.

A common feature is noticed in reviewing the literature on c-BN deposited using PVD. That is, the c-BN phase is being created by "brute force" under the influence of surface bombardment with highly energetic ions of nitrogen and argon.¹ In contrast, the techniques applying CVD are more gentle. Chemical reactions are then assumed to be the controlling mechanism on the growing c-BN surface. In this case, B- and N-containing precursors are being used in the gaseous mixture, which diffuse to, and self-assemble on, the growing c-BN surface without the impact of high-energy heavy ions.

The chemical vapor deposition technique is one example of a thin film technique which involves chemical reactions in both the gaseous phase and on the growing surface. Vapor growth of thin films is a dynamic process with a large degree of complexity. It involves the generation of surface vacancies by gaseous species and adsorption of terminating species (e.g., H), as well as of growth species. This complex dynamic process is also assumed to include surface processes like migration. It is very important to obtain a deeper knowledge at the molecular level of these surface processes. This is especially true for the optimization of the deposition process. One important factor is the energetics during the growth. Adsorption and abstraction

energies, as well as barrier energies for migration, are then especially interesting to study.

There are important industrial and technical applications for c-BN compounds. This is mainly due to their extraordinary chemical and physical properties (e.g., extreme hardness, high thermal conductivity and electric resistivity, large band gap, chemical inertness). Cubic boron nitride possesses also a high thermal stability, both in oxidizing environments and in contact with Fe, Co, and Ni. It is, hence, promising as a tool coating for machining of steel, cast iron, and ferrous alloys. Furthermore, c-BN can be made as both n- and p-type semiconductors, suitable for p-n junction diodes. However, there are current problems in the CVD synthesis of c-BN. This is, at first, surprising since the cubic phase of c-BN is the thermodynamical most stable phase.

Bartl et al.² have presented some conditions to achieve a successful c-BN formation using CVD. They include (i) stabilization of the c-BN surface during growth, (ii) sufficient high mobility of the precursor at temperatures in the stability range of c-BN, (iii) preferential etching of h-BN and other "non-c-BN phases", and (iv) preventing secondary nucleation of h-BN during growth of c-BN. The purpose of the present study is to theoretically investigate the thin film CVD growth of c-BN. Stabilization of the B(111) surface, as well as adsorption and migration processes occurring on that very surface during thin film growth, will then especially be investigated. The results will also be compared with corresponding processes occurring during growth of (111) surfaces of diamond.

Method

The Schrödinger equations for the models of adsorption, abstraction, and surface migrations were solved using the ab initio molecular orbital (MO) method at the MP2 order of theory (Möller–Plesset perturbation theory of second order).³ The adsorption and abstraction energies were calculated by using

$$E_{\text{ads,A}} = E_{\text{M-A}} - (E_{\text{A}} + E_{\text{M}}) \quad (1)$$

and

$$E_{\text{abstr,AB}} = (E_{\text{M}} + E_{\text{AB}}) - (E_{\text{M-A}} + E_{\text{B}}) \quad (2)$$

E_A , E_B , E_M , and E_{M-A} are the total energies for the different gaseous species and for the template M with and without an adsorbed species, respectively. E_{AB} is the total energy for the gaseous molecule obtained as a result of the abstraction reaction.

Migration barriers are normally more difficult to calculate compared to the energy of adsorption to a surface radical site. This is mainly due to the problem with the location of the transition state. In the present study, the following procedure was used in locating the transition state. First, the position of the projected transition state on the axis intersecting two chemisorbed species (adsorbed to the two neighboring radical surface sites) was determined by calculating a potential path along this very axis. The potential energies obtained were then least-squared fit to a parabola whose maximum was situated at the midpoint of this intersecting axis. Second, the more exact barrier for migration was obtained by performing a similar procedure but perpendicular (and from above) to the intersecting axis at the position of the first obtained potential energy maximum. The activation energy for the different migrating species was then calculated as the difference in energy for the transition states and the chemisorbed states.

A necessary condition for obtaining a good description of the electronic state of the reactants and products in the present investigation is primarily to choose a model cluster describing the diamond surface well, to perform geometry optimizations, and to choose a highly flexible basis set. It was concluded in earlier investigations by the present authors that a medium-sized template $C_{13}H_{21}$ is adequate to use in the study of the adsorption reactions of hydrogen, hydrocarbons, and fluorine, respectively, on a diamond (111) surface.^{4,5} This conclusion is also expected to be valid for similar adsorption and abstraction reactions occurring on a c-BN (111) surface. For the different templates modeling the (111) surfaces, with or without an adsorbed (or a migrating) species, different atoms were allowed to be relaxed. These atoms are marked in Figure 1. Other underlayer atoms were kept fixed in order to hold the characteristics of the crystal.

A larger template is used when investigating the migration processes (Figure 1b). The framework of this specific template is different in that two neighboring radical surface sites have identical environments, five adjacent H species and one adjacent dangling bond. These types of surface vacancies are assumed to exist under low-pressure growth conditions. Migration of the chemisorbed species is then assumed to occur as a simple jump between the two identical radical surface sites. It is generally known that adsorption of gaseous species to the diamond (111) surface is not especially size-dependent due to the very localized covalent bonds. A question arises if the same is true also for c-BN. As a check, a six-layer thick slab with periodic-boundary conditions was used in studying the effect of size (and number of atoms allowed to be relaxed) on the adsorption of H species on the B(111) surface of c-BN. A supercell approach was then used. The six-layer slab was included in a unit cell with vacuum regions of 18 Å in the (001) direction, while keeping the periodicity in the (100) and (010) directions. A number of three layers of carbons were then allowed to relax in the six-layer thick slab, also including the surface-terminating H atoms. For the medium-sized cluster only the radical carbon atoms were allowed to relax. As a result, the difference in adsorption energy obtained for the two different models was 40 kJ/mol (a difference of less than 10%). Since the aim with the present investigation is to study the order of adsorption and barrier energy, respectively, for different species used, with the

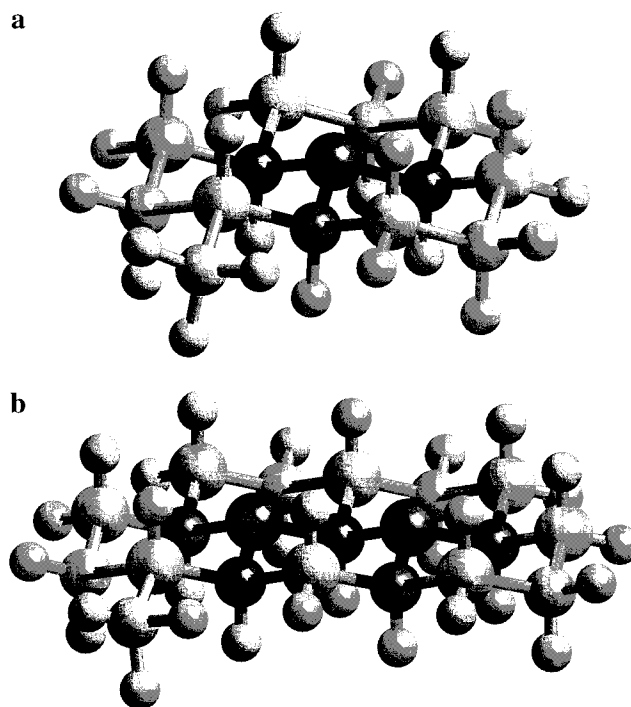


Figure 1. Templates demonstrating the various models used in the present study. The smaller one is used for the surface stabilization study, as well as for the abstraction and adsorption study, respectively. The larger one is used when studying the surface migration of specific growth species. The atoms allowed to be geometrically relaxed are marked in the templates.

numerical differences in adsorption energies larger than 100 kJ/mol, it will be adequate to use the smaller model in the present calculations.

The split-valence basis set with polarization functions (6-31G**) was found necessary to be used in the *ab initio* MO calculations in an earlier work by the present authors.⁵ The adsorption of the halogens F and Cl to an F- and Cl-terminated diamond (111) surface, respectively, were then investigated. The basis set 6-31G**, described in ref 3, also has to be used in the present investigation since c-BN is a polar compound. The split-valence basis sets are able to give an improved description of expansion or contraction of the valence shell in response to differing molecular environments. Furthermore, by addition of polarization functions the description of the charge rearrangement occurring around the atoms will be better.

Results and Discussion

A. Surface Stabilization. Common to all of the ordinary CVD methods are dilute mixtures of simple growth species in an excess of a reactive surface terminating species. H and F have generally been considered to be very important reactants for diamond growth since one of its dominant roles during the growth process is to maintain the sp^3 configuration of the surface carbon atoms.⁵⁻⁸ The stability of various halogenated diamond (111) surfaces has been investigated theoretically in ref 5. These calculations showed that hydrogen, H, and the halogen F and Cl species may sustain the bulk sp^3 structural configuration of the surface carbon atoms. The adsorption energy of F to an F-terminated diamond (111) surface was found to be very similar to the corresponding adsorption energy of H to an H-terminated surface. Furthermore, it was expected that F- and H-terminated diamond (111) surfaces should passivate surfaces from being chemically attacked better than, for instance, Cl- or Br-terminated surfaces do.

TABLE 1: Calculated Adsorption and Abstraction Energies on the MP2 Level of Theory^a

	ads energy (kJ/mol)	abstr energy (kJ/mol)
H-terminated	−442 (H)	+18 (H)
	$\nu_{\text{N-B-N}} = 110.0^0$	−104 (F)
F-terminated	−653 (F)	+108 (H)
	$\nu_{\text{N-B-N}} = 111.7^0$	+512 (F)

^a The species within parentheses are gaseous species assumed to be adsorbed or used in the abstraction reaction. Angles formed by B_{Surface} and two of its binding N neighbors are also shown.

Cubic BN growth is more complicated due to its binary nature. The planes consists of either B or N atoms (Figure 1). This will most probably lead to restrictions in the thin film growth. These planes will hereafter be referred to as B(111) and N(111), respectively.

Widany et al.⁹ have performed MD simulations of clean (nonterminated) c-BN (111) surfaces at room temperature. Transformation to sp² hybridization, rather than reconstruction, similar to clean diamond (111), was then observed. However, the effect of the transformation of hybridization was much weaker in the case of a B(111) compared to a N(111). The influence of the addition of hydrogen to the gas phase of an inductively coupled plasma CVD process to deposit c-BN was investigated by Kuhr et al.¹⁰ It was found that H₂ in addition to the hydrogen introduced with the source gas trimethylborazine prevents the formation of c-BN but not that of the sp² nucleation layer. The surface structures of single-crystal c-BN (100) and (111) have been exposed to argon-ion sputtering and then to a prolonged exposure of hydrogen plasma in a work by Loh et al.^{11,12} The low-energy argon-ion sputtering of c-BN (100) resulted in local disruption on the surface (from sp³ to sp²-type bonding). An additional H-etching resulted in a H-terminated and restructured c-BN (100)-(2 × 1) surface with sp³-type bonding. A prolonged exposure in H plasma lead to a H-terminated (111)-(1 × 1) surface. Furthermore, the (100) surface was, as a result of a prolonged exposure with H, etched to become an unreconstructed (111) surface. In a work by Bohr et al.,¹³ the influence of F₂ on c-BN in thermodynamic equilibrium was found to be similar to that of atomic hydrogen. Hence, the reaction of F₂ with the solid phase is thermodynamically possible.

The challenge in the CVD process is now to find a way to stabilize the c-BN surface and to suppress the formation of h-BN that is equivalent to the use of atomic hydrogen (or fluorine) in diamond CVD. The stabilizing effects of H, as well as of the halogens F, Cl, and Br, on c-BN cluster surfaces have in a recent study been investigated structurally and energetically by performing quantum mechanical calculations.¹⁴ It was then found that F species will be efficient in stabilizing the two different types of (111) cluster surfaces, N(111) or B(111). The H species was, however, only found to be effective as a stabilizing agent in the case of a B(111) surface. All atoms in the clusters were allowed to be totally geometrically relaxed in the calculations.

The aim of the present study is to investigate the corresponding stabilizing efficiency of H and F, respectively, for a template modeling the (111) terrace of c-BN. As can be seen in Table 1, the calculated adsorption energy for F shows that this species will (compared to H) be much stronger bonded to the surface (653 vs 442 kJ/mol). The angles formed by the surface B atom and two of its binding neighbors ($\nu_{\text{N-B-N}}$) are also shown in Table 1 for the different adsorption processes. This angle is expected to be numerically close to the tetrahedral angle (109.4) for a sp³-hybridized surface atom. The angles obtained for the

H- and F-terminating surfaces in the present investigation are 110.0 vs 111.7. Especially the former one is rather close to the tetrahedral angle. For the latter one, there is a minor influence of sp² hybridization. Both the large adsorption energies for H and F, and the optimized structural geometries for the closest environments to the adsorbates, will hence support the conclusion that F, as well as H, will be effective in stabilizing the c-BN B(111) surface; i.e., protect the sp³-hybridized surface atoms from being sp²-hybridized to any larger extent. However, the B(111) surface has a more pronounced tendency to become terminated by F species due to the larger adsorption energy of F compared to H.

As expected from the large difference in electronegativity of F, on one hand, and H, on the other, the fluorine atom will induce a much larger atomic charge rearrangement near the surface with a large depletion of charge from the surface borons and, hence, an appreciable ionic character of the B–F chemical bond. This charge rearrangement in the structural region of adsorption is then reflected in the much larger adsorption energy of F to an F-terminated surface compared to the adsorption of H to an H-terminated surface. Stabilization of the c-BN surface during growth is one of the conditions that according to Bartl et al.² has to be fulfilled in order to achieve successful c-BN formation.

B. Abstraction of Terminating Species. Different abstraction reactions have been investigated in the present study. It should be emphasized that all energies for reactions are calculated at 0 K. Both the H- and F-terminated B(111) surface were then assumed to undergo abstraction reactions including gaseous H or F species. As can be seen in Table 1, the energetically most favorable abstraction reactions involved surface-terminating H species. An abstraction of H species by gaseous F was found to be the most exothermic process (−104 kJ/mol). This is to be compared with the endothermic abstraction of surface-terminating F species with gaseous H (+108 kJ/mol). The energetically least favorable abstraction reaction included no hydrogens. The abstraction of surface-terminating F species by gaseous F was in fact an extreme endothermic process (+512 kJ/mol). The numerical value of the abstraction energy for the corresponding process including only H species was situated somewhere between these above presented extremes (+18 kJ/mol). This is a weakly endothermic process at 0 K, which, however, will be possible to occur at higher temperatures and at the supersaturation condition of hydrogen in the chemical vapor deposition of c-BN thin films.

On the basis of this energetic investigation, it is possible to draw the conclusion that an H-terminated c-BN B(111) surface will be energetically favorable in abstraction reactions including gaseous H and F species, respectively.

C. Adsorption of B- vs N-Containing Growth Precursors. Mixtures of boron-containing precursor and nitrogen (or ammonia) have generally been applied for c-BN deposition.¹ Diborane, B₂H₆, is widely used as a boron-containing precursor. Other examples include boron chloride^{2,15} and boron fluoride.¹⁶ The BF₃/N₂/H₂ gas mixture was successfully used to deposit B_xN_x films under CVD conditions in a work by Hentschel et al.¹⁷ Single-source precursors have also been used.¹ One major difference between a single-source precursor and, e.g., NX₂ (X = H, F) is that the former species contains both B and N, being a growth species for growth of two layers simultaneously. When using NX₂ as a growth species, only an N(111) surface is possible to grow. A boron-containing species also has to be introduced into the CVD reactor in order to be able to grow a second layer of c-BN B(111).

TABLE 2: Calculated Adsorption and Barrier Energies on the MP2 Level of Theory^a

	ads energy (kJ/mol)	barrier energy (kJ/mol)
H-termination	459 (NH ₂)	120 (BH ₂)
	201 (NF ₂)	276 (NH ₂)
	394 (BH ₂)	
	412 (BF ₂)	
F-termination	416 (NH ₂)	
	17 (NF ₂)	
	353 (BH ₂)	
	327 (BF ₂)	

^a The species within parentheses are the gaseous species that are adsorbed or migrating on the surface.

One of the purposes with the present investigation is to study the adsorption process of NX₂ and BX₂ species on the B(111) surface of c-BN. In a comparison of the CVD of diamond and c-BN it will be of a large interest to study the corresponding adsorption processes for diamond as well by using the gaseous species CH₂ instead of NH₂ or BH₂. The CH₂ species have earlier been found to be strongly bonded to an H-terminated diamond (111) surface (364 kJ/mol).⁴ This species is found to be present in the gas phase during typical diamond CVD growth conditions.

As was shown in section 3 (Surface Stabilization), a mixture of F and H species in the gas phase will result in energetically favorable abstraction reactions. It will then be of a large interest to study also the effect of F (versus H) on the adsorption reactions during thin film growth of c-BN.

The calculated adsorption energies for adsorption of NX₂ and BX₂ to an H- and F-terminated c-BN B(111) surface, respectively, are shown in Table 2. The species were all found to be more strongly bonded to an H-terminated surface. The following order of adsorption energies were obtained for the NX₂ species: NH₂ (H) > NF₂ (H) > NH₂ (F) > NF₂ (F) (459 > 201 > 201 > 17 kJ/mol). The parentheses indicate the type of surface termination. The NH₂ species adsorbed on a H-terminated surface is the most strongly bonded one in the present investigation (459 kJ/mol). It is even more strongly bonded to the surface compared to the H species (442 kJ/mol). The NF₂ species adsorbed on an F-terminated surface was found to be the weakest bonded one in the present investigation (17 kJ/mol). One of the reasons for the smaller adsorption energy obtained for the F-terminated surface is most probably the sterical hindrances induced by the larger F atoms (both in NF₂ and on the surface) (Figure 2). A bonding situation in which the gaseous species BX₂ will be bonded to the B(111) surface of c-BN will, hence, result in a much smaller range of adsorption energies compared to the corresponding adsorption of NH₂ (range of 85 vs 442 kJ/mol). The following order of adsorption energies were obtained for the BX₂ species: BF₂ (H) > BH₂ (H) > BH₂ (F) > BF₂ (F) (412 > 394 > 353 > 327 kJ/mol). As can be seen in Table 2, the adsorption of BX₂ to an F-terminated surface will result in much larger bond strengths compared to the adsorption of NX₂ to a F-terminated surface. On the contrary, the adsorption of BX₂ to an H-terminated surface will result in somewhat smaller adsorption energies compared to the adsorption of NX₂ to a H-terminated surface. As a conclusion drawn from these energetical calculations, a mixture of the boron- (BX₂) and nitrogen-containing (NX₂) species in the gas phase during chemical vapor deposition of c-BN thin films will most probably result in a mixture of these species as well on the B(111) surfaces. This is an unfavorable result since only nitrogen-containing species are the expected growth precursors on this type of surface. The situation is even worse for a F-terminated surface, for which the boron-containing

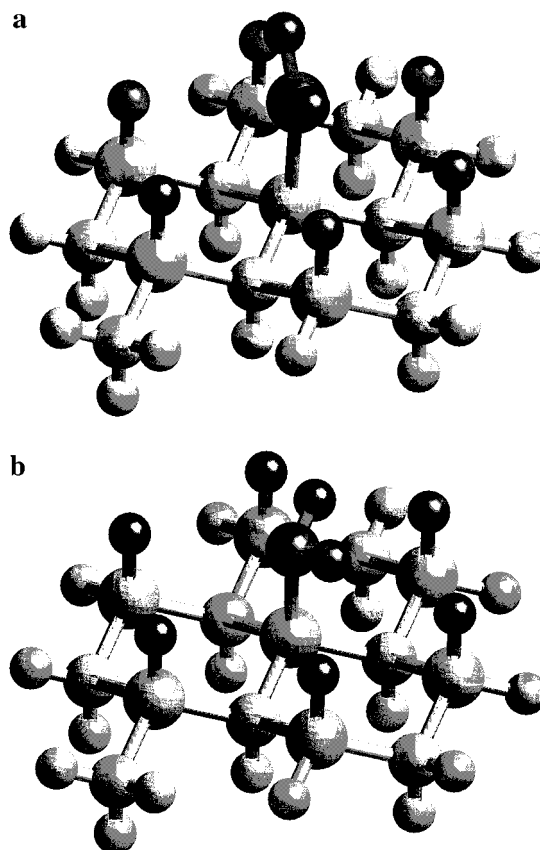


Figure 2. Templates demonstrating the bonding geometries for (a) BX₂ and (b) NX₂ (X = H, F) adsorbed on the c-BN B(111) surface.

species (BX₂) was found to energetically be much more strongly bonded to the surface compared to the nitrogen-containing species (NX₂).

In the present investigation, the adsorption of the NH₂ and BH₂ species, respectively, on the H-terminated c-BN B(111) surface did result in adsorption energies (equivalent to binding energies) numerically very similar to the corresponding adsorption of CH₂ (459 and 394 vs 416 kJ/mol) on an H-terminated diamond (111) surface.⁴

D. Surface Migration of Adspecies. Growth of diamond has usually been discussed without including explicitly the possibility for surface diffusion. Past mechanistic studies¹⁸ have usually presumed that the growth of diamond takes place by a direct, Eley–Rideal type mechanism. A gaseous precursor then undergoes a chemical reaction immediately upon its collision with a reactive surface site or, if the reaction cannot take place, scatters away from the surface. The main reason for this assumption is that the carbon-containing precursors are forming very strong covalent bonds with the surface, and the probability for surface diffusion is, hence, expected to become very low. However, a stepped morphology on the surface has been shown to be characteristic of chemical vapor deposited diamond,¹⁹ and earlier experiments have indicated that surface diffusion can take place during diamond growth.²⁰ For such a case, growth of diamond should occur through propagation of steps over the diamond surface. The complex dynamic processes occurring during chemical vapor deposition of diamond is, hence, also assumed to include surface processes such as migration of surface-terminating species (e.g., H, F) and different types of growth species. Due to the large chemical and physical similarities between diamond and c-BN, this assumption is in the present investigation also assumed to be valid for c-BN. As was discussed by Bartl et al.,² the challenge in the CVD of c-BN

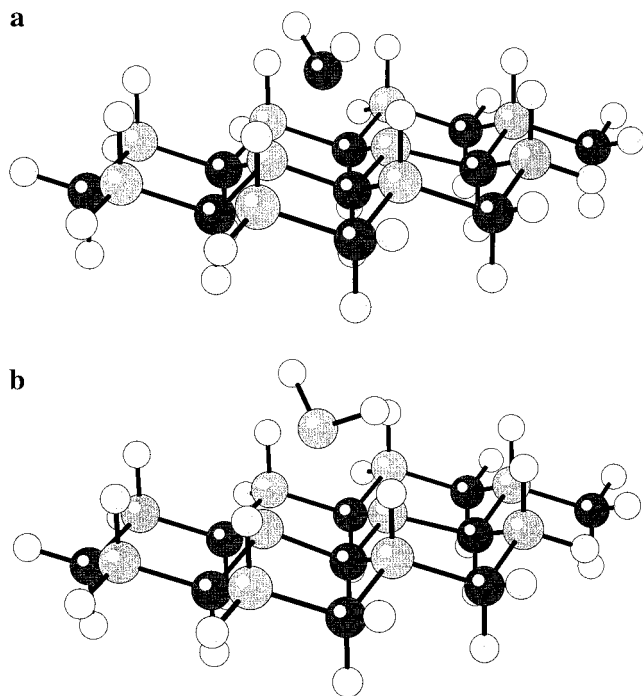


Figure 3. Templates demonstrating the geometry of transition states for (a) NH_2 and (b) BH_2 for an assumed single jump between two neighboring surface B atoms.

is to grow the stable phase by either suppress the nucleation of h-BN or to favor the nucleation of c-BN. A high mobility of the growth precursors (e.g., NH_2) is then needed for the continuous growth of the stable c-BN phase.

As was discussed in section 2 (Methods), the migration processes investigated in the present study are assumed to involve two neighboring surface radical sites (Figure 1b). On the basis of the energetically favorable abstraction reactions presented and discussed in section 4 (Abstraction of Terminating Species), the H-terminated part of the c-BN B(111) surface will most probably contain this diradical type of surface sites. Migration of NH_2 and BH_2 is then assumed to occur as a single jump between the two radical surface sites. The migration will be of an anisotropic character since every surface boron has six symmetrically equivalent boron neighbors on the surface (Figure 1).

As can be seen in Table 2, the NH_2 species has a somewhat larger tendency (compared to BH_2) for adsorption to a mono-radical H-terminated c-BN B(111) surface (adsorption energy of 459 vs 394 kJ/mol). On the other hand, the smallest barrier of energy in the present investigation is obtained for the BH_2 species (120 (BH_2) vs 276 (NH_2) kJ/mol). These barriers of energies are relatively large and will thus prevent an adsorbed NH_2 (or BH_2) species to move more or less freely over the surface. The barriers of migration are, however, considerable more energetically favorable (by about 183 (NH_2) and 274 (BH_2) kJ/mol) compared to any desorption process. The geometries of the transition states are shown in Figure 3. The distances obtained between the N atom in NH_2 and the B atom in BH_2 and one of the radical surface boron atoms are for these migrating species 2.04 vs 2.26 Å.

The energy barriers obtained in the present study differ considerably from those obtained in a corresponding investigation for diamond.²¹ The barrier energy obtained for the migration of CH_2 on diamond (111) was much smaller than for the migration of NH_2 and BH_2 , respectively, on the B(111) surface of c-BN (52, 276, and 120 kJ/mol). The calculations show that

the CH_2 species binds strongly to the diamond surface at the geometry of transition state. Two single bonds are then formed between the triplet state of CH_2 and each of the two radical surface carbons by overlapping dangling bonds. This is not the situation for the corresponding geometry of the NH_2 and BH_2 species, respectively, on the c-BN surface.

Furthermore, the geometry of the CH_2 species at the transition state is not identical to the geometry for the chemisorbed state. The H-C-H angle for the transition state is about 120° , being less than 180° which was the corresponding angle for the chemisorbed state. The geometries of the BH_2 and NH_2 species at their respective transition states are also not identical to the corresponding chemisorbed geometries. The H-B-H (H-N-H) angles for the transition states are 110° (106°) compared to 119° (110°), which is valid for the chemisorbed states.

Summary

Different types of abstraction and adsorption reactions, as well as surface migration processes, have theoretically been investigated for the B(111) surface of c-BN. As a result, both F and H will be effective in stabilizing the B(111) surface of c-BN. This result is in agreement with a corresponding investigation for diamond (111). However, the F-stabilized surfaces have in the present investigation been shown to be resistant to abstraction and further growth of c-BN. The smallest probability for adsorption of growth species occurred on the F-terminated part of the surface. Moreover, the boron-containing species (BX_2) was then, unfortunately, found to energetically be much more strongly bonded to the surface compared to the nitrogen-containing species (NX_2). The strongest adsorption occurred on the H-terminated areas of the surface. However, a mixture of B- and N-containing species adsorbed on B(111) will most probably be the result from a corresponding mixture in the gas phase.

The present investigation will, hence, support the conclusion that a gaseous mixture including the halogen F- and the B-containing growth species, BX_2 , has to be avoided in order to be successful in the deposition of a second N(111) layer on top of a B(111) layer. Moreover, the adsorption energies of BH_2 and NH_2 were numerically found to be almost identical with the adsorption energy obtained for the adsorption of CH_2 to the (111) surface of diamond.

The mobility of NH_2 and BH_2 on the H-terminated B(111) surface of c-BN was also investigated by calculation of barrier energies for a single jump process between neighboring surface boron atoms. The results suggest that the mobility of NH_2 and BH_2 on c-BN (111) is much smaller than the mobility of CH_2 on diamond (111) at growth temperatures.

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